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[Document] Description

[Title of the Invention]

Hydrogen Supply System

[Technical Field]

[0001]

The present invention relates to a hydrogen supply system for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile.

[Background Art]

[0002]

Recently, as measures for problems of environment and natural resources, development of a fuel cell automobile is actively pursued. As a fuel cell automobile, a fuel cell automobile loading a container storing hydrogen in the form of a hydrogen gas or a hydrogen storage alloy is being developed, but an important problem in its spread is improvement of hydrogen supply infrastructure. That is, how to improve the wide-area hydrogen supply infrastructure for freely running fuel cell automobiles is the problem. Then, a system in which a utility gas or a liquid fuel (desulfurized naphtha, gasoline, lamp oil, diesel oil, methanol, etc.) is steam-reformed by a reforming device at a hydrogen supply station and is stored in a hydrogen storage tank, and the hydrogen is supplied to a hydrogen storage container loaded on a fuel cell automobile is the most actively developed since it has a merit that an existing infrastructure such as a utility gas piping network, a gas station and the like can be utilized at the maximum (See Patent Documents 1 to 3, for example).

However, the above-described hydrogen supply system has

problems that the reforming device is expensive, the device size is large or maintenance and operation thereof is complicated and requires an advanced technology.

[Patent Document 1] Japanese Unexamined Patent Application Publication No. 2002-315111

[Patent Document 2] Japanese Unexamined Patent Application Publication No. 2002-337999

[Patent Document 3] Japanese Unexamined Patent Application Publication No. 2003-118548

[Patent Document 4] Japanese Unexamined Patent Application Publication No. 2004-79262

[0003]

Also, as the reforming device, development of a reforming device of methanol with the lowest reforming temperature is advanced, and three methods of steam reforming, partial oxidization reforming and reforming using both are employed (See Non-Patent Document 1), but in any reforming method, in order to produce a hydrogen containing gas, reforming should be carried out at a temperature as high as 200°C or more, and there are problems of poisoning of reforming catalyst, removal of CO contained in the reformed gas (gas including hydrogen), mixture of nitrogen in the air into the reformed gas obtained by partial oxidization reform or reform using the both methods.

[Non-Patent Document 1] "Development and Practical Application of Solid Polymer type Fuel Cell", PP 141 to 166, May 28, 1999, issued by Technical Information Institute, Co., Ltd.

[0004]

On the other hand, such a system in which water is electrically decomposed to generate hydrogen instead of reforming a fuel containing an organic compound as above, this hydrogen is stored in a hydrogen storage tank and supplied to a hydrogen storage container loaded on a fuel cell automobile is under development (See Patent Documents 5 and 6, for example).

According to this system, though a high temperature to reform a fuel containing an organic compound is not needed, there is a problem that a large volume of electric power is required.

[Patent Document 5] Japanese Unexamined Patent Application Publication No. 2002-161998

[Patent Document 6] Japanese Unexamined Patent Application Publication No. 2002-363779

[Disclosure of Invention]

[Object of the Invention]

[0005]

With a view to give a solution to the above problems, the present invention aims to provide a hydrogen supply system using a hydrogen generating device which can easily supply hydrogen to a hydrogen storage container loaded on a fuel cell automobile, produce a hydrogen-containing gas at a low temperature, and moreover, requires no large electric energy.

[Means for Achieving the Object]

[0006]

Proposed to give a solution to the problems, the present invention can be reduced to the following constitutive elements.

(1) A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, the system characterized in that the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound at a temperature of 100°C or lower.

(2) The hydrogen supply system according to the above section (1), characterized in that the hydrogen generating device produces a hydrogen-containing gas by decomposing a fuel containing an organic compound at a temperature of 30 to 70°C.

(3) The hydrogen supply system according to the above section (1) or (2), characterized in that the hydrogen generating device produces a hydrogen-containing gas without supplying electric energy from outside to a hydrogen generating cell composed of a partition membrane.

(4) The hydrogen supply system according to the above section (1) or (2), characterized in that the hydrogen generating device produces a hydrogen-containing gas while withdrawing electric energy from a hydrogen generating cell composed of a partition membrane.

(5) The hydrogen supply system according to the above section (1) or (2), characterized in that the hydrogen generating device produces a hydrogen-containing gas while providing electric energy from outside to a hydrogen generating cell composed of a partition membrane.

(6) A hydrogen supply system provided with hydrogen

supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, the system characterized in that the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound and comprises a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the organic compound, and means for supplying an oxygen-containing gas on the other surface of the partition membrane.

(7) The hydrogen supply system according to the above section (6), characterized in that the hydrogen generating device has no means for supplying electric energy from outside to a hydrogen generating cell constituting the hydrogen generating device.

(8) The hydrogen supply system according to the above section (6) or (7), characterized in that the hydrogen generating device is provided with an oxidizing electrode on a surface of the partition membrane supplying an oxygen-containing gas.

(9) A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, the system characterized in that the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing

an organic compound and comprises a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the organic compound, an oxidizing electrode provided on the other surface of the partition membrane, and means for supplying an oxygen-containing gas to the oxidizing electrode, and means for withdrawing electric energy with the fuel electrode serving as a negative electrode and the oxidizing electrode as a positive electrode.

(10) A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, the system characterized in that the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound and comprises a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the organic compound, an oxidizing electrode provided on the other surface of the partition membrane, and means for supplying an oxygen-containing gas to the oxidizing electrode, and means for providing electric energy from outside with the fuel electrode serving as a positive electrode and the oxidizing electrode as a negative electrode.

(11) The hydrogen supply system according to any one of the above sections (8) to (10), characterized in that the hydrogen generating device adjusts the evolution volume of the hydrogen-containing gas by controlling an open-circuit voltage

or an operation voltage between the fuel electrode and the oxidizing electrode.

(12) The hydrogen supply system according to the above section (11), characterized in that the open-circuit voltage or operation voltage is adjusted to 300 to 600 mV.

(13) The hydrogen supply system according to the above section (11) or (12), characterized in that the open-circuit voltage or operation voltage is adjusted by controlling the supply volume of the oxygen-containing gas.

(14) The hydrogen supply system according to any one of the above sections (11) to (13), characterized in that the open-circuit voltage or operation voltage is adjusted by controlling the concentration of oxygen in the oxygen-containing gas.

(15) The hydrogen supply system according to any one of above sections (11) to (14), characterized in that the open-circuit voltage or operation voltage is adjusted by controlling the supply volume of the fuel containing an organic compound.

(16) The hydrogen supply system according to any one of above sections (11) to (15), characterized in that the open-circuit voltage or operation voltage is adjusted by controlling the concentration of the fuel containing an organic compound.

(17) The hydrogen supply system according to any one of the above sections (11) to (16), characterized in that the open-circuit voltage or operation voltage is adjusted by controlling the electric energy to be provided or the electric energy to be withdrawn.

(18) The hydrogen supply system according to any one of above sections (6) to (17), characterized in that the partition membrane is a proton conducting solid electrolyte membrane.

(19) The hydrogen supply system according to the above section (18), characterized in that the proton conducting solid electrolyte membrane is a perfluorocarbon sulfonate-based solid electrolyte membrane.

(20) The hydrogen supply system according to any one of the above sections (6) to (17), characterized in that the partition membrane is an oxygen-soluble polymer membrane.

(21) The hydrogen supply system according to any one of the above sections (6) to (20), characterized in that a catalyst of the fuel electrode is made of platinum-ruthenium alloy supported by carbon powder serving as a base.

(22) The hydrogen supply system according to any one of the above sections (8) to (21), characterized in that a catalyst of the oxidizing electrode is made of platinum supported by carbon powder serving as a base.

(23) The hydrogen supply system according to any one of the above sections (1) to (22), characterized in that the fuel containing an organic compound is an aqueous solution containing methanol.

(24) The hydrogen supply system according to any one of the above sections (1) to (23), characterized by comprising means for circulating the fuel containing an organic compound.

(25) The hydrogen supply system according to any one of the above sections (1) to (24), characterized in that a carbon dioxide absorbing portion for absorbing carbon dioxide

contained in the generated hydrogen-containing gas is provided.

[0007]

Here, the hydrogen generating device has the means for supplying a fuel and a gas containing oxygen, such as a pump or a blower. Also, the hydrogen generating device may have the discharge control means for withdrawing electric energy from the hydrogen generating cell. Further, the hydrogen generating device has the electrolytic means for providing electric energy to the hydrogen generating cell. Moreover, the hydrogen generating device has a function to control the supply volume or concentration of these gases and the electric energy to be withdrawn or to be provided by monitoring the open-circuit voltage or operation voltage of the hydrogen generating cell. The basic construction of the hydrogen generating cell constituting the hydrogen generating device is that the fuel electrode is provided on one surface of the partition membrane, allowing for supply of fuel to the fuel electrode, while allowing for supply of the oxygen-containing gas to the other surface of the partition membrane. Such construction may include the oxidizing electrode on the other surface of the partition membrane.

Also, the fuel cell automobile is not limited to those obtaining a driving force of the vehicle only by a fuel cell but includes a hybrid car also using another power source.

[Advantage of the Invention]

[0008]

Since the hydrogen supply system of the present invention uses the hydrogen generating device that can reform the fuel at 100°C or less from a room temperature, which is extremely

lower than the conventional reforming temperature, both time required for start and energy amount to raise the temperature of a reformer can be reduced. Also, such an effect is exerted that hydrogen can be supplied easily to the fuel cell. Further, the hydrogen generating device can produce hydrogen without supplying the electric energy from outside to the hydrogen generating cell. Moreover, a process control is made possible by monitoring the voltage of the hydrogen generating cell and the size of the hydrogen generating device can be reduced, which can also reduce the manufacturing costs of the hydrogen supply system.

If the means for withdrawing electric energy is provided in the hydrogen generating device, the electric energy can be used for operating the pump, blower or other auxiliary machines, and its effect is great in terms of effective utilization of energy.

Even if the means for providing electric energy from outside is provided, by supplying a small amount of electric energy from outside to the hydrogen generating cell, hydrogen larger than the inputted electric energy can be generated, which is another effect.

[Best Mode for Carrying Out the Invention]

[0009]

The most preferred embodiments in the execution of the present invention will be illustrated below.

The hydrogen generating device used in the hydrogen supply system of the present invention is basically novel, and the embodiments thereof described herein are given only for the illustrative representation of the invention, and not for

limiting the scope of the invention.

[0010]

The basic construction of the hydrogen supply system of the present invention comprises hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device for generating a hydrogen-containing gas to be supplied to the hydrogen supply means.

FIG. 1 shows an example of a system flow of the hydrogen supply system of the present invention.

Since the hydrogen generating device operates at a low temperature, it is not necessary to provide a heater to raise the temperature as shown in FIG. 1, however, the heater may be provided as necessary.

[0011]

The hydrogen supply means for supplying hydrogen to the hydrogen storage container loaded on the fuel cell automobile comprises, for example, a hydrogen booster machine, a high-pressure hydrogen storage tank, and a hydrogen dispenser.

[0012]

As the hydrogen booster machine, a hydrogen compression pump is generally used, but any device can be used only if the pressure of hydrogen can be boosted. The hydrogen gas pressure at the hydrogen booster outlet is preferably higher in view of a volume efficiency, preferably at 50 atmospheric pressure (5 MPa) or more, more preferably at 100 atmospheric pressure (10 MPa) or more or further preferably at 200 atmospheric pressure (20 MPa) or more. An upper limit is not particularly limited, but 1000 atmospheric pressure (100 MPa) or less is preferable.

[0013]

After the hydrogen-pressure boosting process, a high-pressure hydrogen storage tank is preferably provided for storing hydrogen. As the high-pressure hydrogen storage tank, its form is not particularly limited only if it can withstand the boosted hydrogen, and a publicly known device can be used. Besides a high-pressure hydrogen storage tank for storing a high-pressure hydrogen gas as it is, a high-pressure hydrogen storage tank incorporating a hydrogen storage alloy can be used.

[0014]

The hydrogen gas is guided to the hydrogen dispenser from the high-pressure hydrogen storage tank. Alternatively, the outlet gas of the hydrogen booster can be directly guided to the hydrogen dispenser without going through the high-pressure hydrogen storage tank. In that case, a piping is provided for connecting the hydrogen boosting machine to the hydrogen dispenser.

[0015]

The hydrogen dispenser is to supply a hydrogen gas to the hydrogen storage container of the fuel cell automobile using hydrogen as a fuel, and a publicly known dispenser can be used. This hydrogen storage container may be a hydrogen storage container as loaded on a fuel cell automobile, and if this container can be removed from the fuel cell automobile, it may be the hydrogen storage container in the state removed from the fuel cell automobile.

[0016]

The hydrogen generating cell in the hydrogen generating

device used in the hydrogen supply system of the present invention is basically composed of a partition membrane and a fuel electrode provided on one surface of the partition membrane. As described later, technically this hydrogen generating device does not necessarily require an oxidizing electrode (air electrode); however, it is preferable to provide an air electrode on the other surface of partition membrane. The element configured as described above may be represented by an MEA (membrane/electrode assembly) used in a direct methanol fuel cell.

[0017]

The method for fabricating an MEA is not limited to any specific one, but a method similar to a conventional one may be employed in which a fuel electrode and an air electrode with a partition membrane inserted therebetween are compressed at a high temperature to be assembled.

[0018]

Suitable partition membranes may include an oxygen-soluble polymer membrane and a proton conducting solid electrolyte membrane which has been used as a polymer electrolyte membrane of a fuel cell. The proton conducting solid electrolyte membrane preferably includes a membrane based on perfluorocarbon sulfonate having sulfonic acid group such as Nafion provided by Dupont. Further, not only the proton conducting membrane but also an ion conducting membrane is likely to be applicable. Moreover, a partition membrane formed from inorganic material such as ion conducting glass may be used.

[0019]

It is considerable that the oxygen-soluble polymer membrane is used when the hydrogen generating device for use in the hydrogen supply system of the present invention is, in principle, a partial oxidizing reformer. More specifically, the oxygen-soluble polymer membrane is conceivably the material for a soft contact lens composed of polyhydroxymethacrylate (moisture content of 36%), hydroxymethacrylate and n-vinyl pyrrolidone copolymer (moisture content of 78%), a silicon film containing no water, a poly(TMSP) film, a thin film containing, at a high mixing rate, cobalt porphyrin capable of adsorbing/desorbing oxygen very swiftly, in a polymer containing vinyl aromatic amine, and a polymer compound film including alternate oligosiloxane chains and oligo-oxyalkylene chains.

[0020]

The fuel electrode or air electrode is preferably an electrode which is conductive and has a catalytic activity. For example, production of such an electrode may be achieved by applying a catalyst paste onto a gas diffusion layer and drying the paste, in which the paste is comprised of a catalyst with carbon powder supporting on a carrier, a binding agent such as a PTFE resin, and an ion conductivity conferring substance such as Nafion solution.

The gas diffusion layer is preferably made of a carbon paper treated to be water-repellent.

The catalyst to be applied to fuel electrode is not limited to any specific one, but is preferably a platinum-ruthenium alloy.

The catalyst applied to air electrode is not limited to

any specific one, but is preferably platinum.

[0021]

For a hydrogen generating device configured as described above, when organic compound-containing fuel such as an aqueous solution containing methanol is supplied to the fuel electrode, and gas containing oxygen is supplied to the air electrode, gas containing hydrogen evolves on the fuel electrode under specified conditions.

[0022]

In the hydrogen generating device used in the hydrogen supply system of the present invention, the hydrogen generating method is quite different from conventional hydrogen generating methods, and it is still difficult at present to explain the mechanism. The hypothesis which is currently thought most likely to be true will be described below, but it can not be denied that the hypothesis would be upset by new reactions.

[0023]

According to the invention, as described above, hydrogen-containing gas evolves, at a temperature as low as 30 to 70°C, from the fuel electrode which receives the supply of methanol and water as will be described below. When no electric energy is supplied from outside to the hydrogen generating cell, gas containing hydrogen at 70 to 80% evolves, while when electric energy is supplied from outside to the cell, gas containing hydrogen at 80% or higher evolves. The evolution of gas depends on the open-circuit voltage or operation voltage between the two electrodes. Base on these results, the most likely explanation of the mechanism underlying the evolution

of hydrogen is as follows.

[0024]

Typically, the following two reactions are considered as a technique of generating hydrogen from methanol:

1) $CH_3OH + 1/2O_2 \rightarrow 2H_2 + CO_2$

2) $CH_3OH + H_2O \rightarrow 3H_2 + CO_2$

[0025]

1) is a reaction called partial oxidation reaction, wherein 1 mol methanol reacts with oxygen to produce 2 mol hydrogen. This reaction is an exothermic reaction, and heat is externally generated as this reaction progresses.

Assuming that this partial oxidation reaction progresses in the hydrogen generating cell employed in the present invention, it is highly likely that the oxygen necessary for the reaction is supplied from the air electrode side of the MEA while being diffused through the electrolyte membrane.

The Nafion used for the electrolyte in the present invention is known for proton conductivity and large diffusion of methanol and water, and is said to be high in oxygen permeability.

Such facts stand for the possibility in the mechanism of hydrogen evolution in the present invention that the methanol in the fuel is partially oxidized with the oxygen which has permeated the electrolyte membrane, thereby evolving hydrogen.

[0026]

Moreover, when electric energy is provided from outside with the fuel electrode serving as a positive electrode and the oxidizing electrode (air electrode) serving as a negative electrode, hydrogen may evolve through electric decomposition.

In that case, hydrogen conceivably could evolve on the fuel electrode side by any reaction below:

3) $H_2O \rightarrow 2H^+ + 2e^- + 1/2O_2$ (air electrode)

$2H^+ + 2e^- \rightarrow H_2$ (fuel electrode)

4) $CH_3OH \rightarrow 4H^+ + 4e^- + CO$ (air electrode)

$4H^+ + 4e^- \rightarrow 2H_2$ (fuel electrode)

However, the above reaction alone cannot produce hydrogen more than the electric energy applied.

[0027]

The meaning of the potential of the cell will be described here. Generally, the voltage of a cell having two electrodes with an electrolyte membrane inserted therebetween is determined by the difference between the two electrodes of chemical potentials of ions which serve as conductors in electrolyte.

That is, since a hydrogen ion-conducting Nafion is used for electrolyte, the voltage in question indicates the difference between the two electrodes of chemical potentials of hydrogen, in other words, partial pressures of hydrogen.

[0028]

In this case, it can be considered that the partial pressure difference of hydrogen represents partial pressure difference of oxygen in balance with the hydrogen partial pressure because two electrodes contain water. In other words, the open-circuit voltage or operation voltage in question is assumed to monitor the oxygen partial pressure on the fuel electrode side in consideration for the air at an oxygen partial pressure of 0. 21 being supplied to the air electrode side.

This can be understandable based on the assumption that, as in an example of the hydrogen generating device to be described later, the above partial oxidation progresses when the open-circuit voltage or operation voltage falls within a certain range, that is, when the oxygen partial pressure of the fuel electrode falls within a certain range.

[0029]

Next, possibility of the event of steam reforming reaction (this conventional expression is expediently employed in the present invention, although the reaction occurs at a temperature of 100°C or lower, producing no steam and therefore the reforming reaction is caused by water, to be exact) represented in the formula 2) will be described.

In the steam reforming reaction, 3 mol hydrogen evolves per mol of methanol. This reaction is an endoergic reaction and therefore requires supply of heat from outside in order to make the reaction continue.

[0030]

The reaction occurring in the hydrogen generating cell of the present invention is comprehensible since the methanol and water as reactants are supplied directly; however, a critical question remains unsolved:

In the case of the partial oxidation reaction described above, change in the oxygen partial pressure on the fuel electrode side is explainable on the assumption that the oxygen is diffused to the fuel electrode. However, in the case of the steam reforming reaction, the cause of the change in the oxygen partial pressure on the fuel electrode side is unexplainable at present.

[0031]

In any event, it is highly likely that hydrogen evolves in the hydrogen generating cell employed in the present invention by any one of the partial oxidation reaction and steam reforming reaction or both reactions.

[0032]

As cited above, it is assumable that any one of the partial oxidation reaction and steam reforming reaction of organic compound-containing fuel, or both of the reactions are occurring in the fuel electrode. Therefore, it is necessary, in order to evolve hydrogen, to provide the fuel electrode on one surface of the partition membrane to supply fuel thereto, and further supply an oxygen containing gas to the other surface of the partition membrane. Nonetheless, it is considered that the oxidizing electrode (air electrode) may not necessarily be provided on the other surface of the partition membrane to be supplied with the oxygen-containing gas. However, as in the case of the hydrogen generating device to be described later, where a methanol-containing aqueous solution is used as an organic compound-containing fuel, the air electrode should preferably be provided.

Moreover, in the case where the hydrogen generating device includes means for withdrawing electric energy with the fuel electrode serving as a negative electrode and the oxidizing electrode serving as a positive electrode or means for providing electric energy from outside with the fuel electrode serving as a positive electrode and the oxidizing electrode serving as a negative electrode, the oxidizing electrode (air electrode) should be provided.

[0033]

According to the hydrogen generating device used in the hydrogen supply system of the present invention, it is possible to decompose organic compound-containing fuel at 100°C or lower to produce a hydrogen-containing gas. It is preferable to produce a hydrogen-containing gas by decomposing organic compound-containing fuel at a temperature in the range of 30 to 70°C.

Incidentally, for a hydrogen generating cell based on conventional reforming technology, the operation temperature should be kept at 100°C or higher. At this temperature range, water will become vapor and organic compound-containing fuel becomes gas, and even when hydrogen evolves under this condition, it is necessary to provide means specifically adapted for separating hydrogen. The system of the present invention is also advantageous in this point.

Indeed, there will arise a problem as described above, when organic compound-containing fuel is decomposed at 100°C or higher. However, the hydrogen generating device used in the hydrogen supply system of the present invention may be operated at a temperature slightly above 100°C if there be need to do so.

[0034]

According to this hydrogen generating device, the evolution volume of hydrogen-containing gas can be adjusted by regulating the open-circuit voltage or operation voltage between the fuel electrode and oxidizing electrode (air electrode) in any case where no electric energy is supplied to the hydrogen generating cell from outside, where electric

energy is withdrawn to outside, and where electric energy is provided from outside.

It is preferable to regulate the open-circuit voltage or operation voltage within the range of 300 to 600 mV.

[0035]

The open-circuit voltage or operation voltage can be regulated by adjusting the supply volume of oxygen-containing gas, the concentration of oxygen in the gas, the supply volume of the organic compound-containing fuel, the concentration of the organic compound-containing fuel, electric energy (current density) to be withdrawn outside and electric energy (current density) to be provided from outside. This allows for the adjustment of the evolution volume of hydrogen-containing gas.

[0036]

As long as based on the putative principle, the organic compound-containing fuel may be a fuel containing a liquid organic compound or a gaseous organic compound. The liquid organic compound should at least contain hydrogen and be decomposable by reaction with oxygen or water. Although there is no restriction, the organic-containing fuel should preferably contain a liquid organic compound such as methanol, ethanol, isopropyl alcohol or dimethyl ether. Aqueous solution of methanol is particularly preferred. The aqueous solution of methanol cited above as a preferred example of fuel is an aqueous solution containing at least methanol and water, and its concentration of methanol at a region where hydrogen-containing gas evolves may be arbitrarily determined as needed. It is also possible to use a fuel containing a gaseous organic compound such as methane or natural gas.

[0037]

For the hydrogen generating device of the present invention, since the fraction of fuel converted into hydrogen is rather small, it is desirable to provide fuel circulating means to improve thereby the fraction of fuel to be converted into hydrogen.

[0038]

The hydrogen generating device used in the hydrogen supply system of the present invention operates at a temperature as low as 100°C or lower, it is possible to attach a carbon dioxide absorbing portion for absorbing carbon dioxide contained in hydrogen-containing gas to the system by simple means.

Next, illustrative examples of producing a hydrogen-containing gas using this hydrogen generating device will be presented. However, the fractions of catalysts, PTFE, Nafion, etc., and the thickness of catalyst layer, gas diffusion layer and electrolyte membrane are not limited to the values cited in the examples, but may take any appropriate values.

[0039]

[Hydrogen generating example 1]

A hydrogen generating cell of the hydrogen generating device has the same structure as that of a representative direct methanol fuel cell (DMFC).

The structure of the hydrogen generating cell is outlined in FIG. 2.

The electrolyte membrane consists of a proton conducting electrolyte membrane provided by Dupont (Nafion 115); and the air electrode is obtained by immersing carbon paper (Toray) in

a solution where polytetrafluoroethylene is dispersed at 5%, and baking the paper at 360°C to make it water-repellent, and coating, on one surface of the paper, air electrode catalyst paste comprised of air electrode catalyst (carbon-supported platinum, Tanaka Precious Metal, TEC10V50E), fine powder of PTFE, and 5% Nafion solution (Aldrich). Thus, the air electrode exists as a gas diffusion layer with air electrode catalyst. In the preparation of the air electrode catalyst paste, the percent contents by weight of air electrode catalyst, PTFE, and Nafion were made 65%, 15% and 20%, respectively. The loading level of catalyst of the air electrode prepared as above was 1 mg/cm^2 in terms of the weight of platinum per unit area.

[0040]

Another carbon paper was similarly treated to be made water-repellent. One surface of the paper was coated with fuel electrode catalyst paste comprised of fuel electrode catalyst (carbon-supported platinum-ruthenium, Tanaka Precious Metal, TEC61E54), fine powder of PTFE, and 5% Nafion solution. Thus, the fuel electrode exists as a gas diffusion layer with fuel electrode catalyst. In the preparation of the fuel electrode catalyst paste, the percent contents by weight of fuel electrode catalyst, PTFE, and Nafion were made 55%, 15% and 30%, respectively. The loading level of catalyst of the fuel electrode prepared as above was 1 mg/cm^2 in terms of the weight of platinum-ruthenium per unit area.

[0041]

The electrolyte membrane, gas diffusion layer with air electrode catalyst and gas diffusion layer with fuel electrode

catalyst were laid one over another to be hot-pressed at 140°C under a pressure of 100 kg/cm^2 so that they were assembled to form an MEA. The MEA prepared as above had an active electrode area of 60.8 cm^2. The thicknesses of air electrode and fuel electrode catalyst layers were practically the same about 30 μm, and the thicknesses of air electrode and fuel electrode gas diffusion layers were similarly the same about 170 μm.

[0042]

The MEA was further provided on its both surfaces with flow passages through which air can flow and fuel can flow, and was enclosed from outside with an air electrode separator and a fuel electrode separator respectively both made of graphite into which phenol resin is impregnated, in order to prevent the leak of gas from the MEA. To further ensure the seal of MEA against the leak of fuel and air, MEA was surrounded with silicon-rubber made packing.

[0043]

The hydrogen generating cell prepared as above was placed in an electric furnace where hot air was circulated. The temperature of the cell was kept at 30 to 70°C, air was flowed at a rate of 0 to 400 ml/min to the air electrode, and 0.5 to 2M aqueous solution of methanol (fuel) was flowed at a rate of 2 to 15 ml/min to the fuel electrode. Then, the voltage difference between the fuel electrode and the air electrode (open voltage), the volume of gas evolved on the fuel electrode and the composition of the gas were monitored and analyzed.

[0044]

First, the flow rate of aqueous solution of methanol

(fuel) to the cell was kept 8 ml/min, and the temperature of air was kept at 30, 50, or 70°C, thereby altering the flow rate of air, and the volume of gas evolving from the fuel electrode was measured. The evolution volume of gas was determined by underwater conversion.

[0045]

The results are shown in FIG. 3.

Evolution of gas from the fuel electrode of the cell was confirmed with reduction of the flow rate of air for all the temperatures tested. The evolution volume of gas becomes high as the temperature is raised. Studies of relation of the open-circuit voltage (open voltage) with the flow rate of air indicate that as the flow rate of air becomes low, the open-circuit voltage of the cell tends to decline.

[0046]

FIG. 4 shows a graph for indicating relationship between the open-circuit voltage and the evolution volume of gas, both adapted from the results of FIG. 3.

From this, it was found that the evolution volume of gas tends to depend on the open-circuit voltage, and that gas evolves when the open-circuit voltage is in the range of 400 to 600 mV. The evolution volume of gas is the highest around 450 mV for all the temperatures tested.

[0047]

Next, fuel was flowed at 8 ml/min and air at 120 ml/min at 70°C, which was the condition where the rate of gas evolution was the highest, to allow gas to evolve, and the concentration of hydrogen in the gas was determined by gas chromatography.

As a result, it was found that the gas contains hydrogen at about 70%.

[0048]

What is important here is that no current or voltage was provided from outside to the hydrogen generating cell of this hydrogen generating example 1. The cell was only connected to an electrometer for monitoring the open-circuit voltage which has an internal impedance of 1 GΩ or higher, while the cell was supplied with fuel and air.

In other words, this hydrogen generating cell converted part of fuel into hydrogen receiving no external energy except for fuel and air.

In addition, conversion of the methanol-containing aqueous solution occurred at a surprisingly low temperature of 30 to 70°C. In view of these facts, the hydrogen generating device of the present invention is likely to be novel.

Moreover, as demonstrated in FIGS. 3 and 4, the evolution volume of hydrogen-containing gas becomes larger as the temperature increases. Therefore, for the conversion, the methanol-containing aqueous solution may be set at a temperature of 70 to 100°C in order to raise the evolution volume of the hydrogen-containing gas.

[0049]

[Hydrogen generating example 2]

The same hydrogen generating cell as that of hydrogen generating example 1 was used. The temperature of the cell was kept at 70°C, and fuel was provided at the flow rate of 2, 8, or 15 ml/min. Then, relations of the flow rate of fuel, the flow rate of air, the evolution volume of gas and open-circuit

voltage with the flow rate of air were shown in FIG. 5.

From the graph it was found that as the flow rate of fuel decreases, the evolution volume of gas becomes larger.

[0050]

FIG. 6 shows a graph for indicating relationship between the open-circuit voltage and the evolution volume of gas, both adapted from the results of FIG. 5.

From this, it was found that the evolution volume of gas depends on the open-circuit voltage, and is the highest around 450 mV for all the fuel flows tested as in hydrogen generating example 1.

[0051]

In this generating example, the highest evolution volume of gas (18.1 ml/min) was obtained at the open-circuit voltage of 442 mV (operation temperature: 70°C; concentration of fuel: 1M; flow rate of fuel: 2 ml/min; and flow rate of air: 100 ml/min). The concentration of hydrogen in the evolved gas was determined by gas chromatography as in example 1, and found to be about 70%.

[0052]

Based on the result above, assuming such a reaction to be a partial oxidizing reaction (2 mol hydrogen evolves from 1 mol methanol), the conversion efficiency of methanol into hydrogen was calculated.

It was found from the result that methanol is likely to be converted into hydrogen with a 14% conversion efficiency. This conversion efficiency cannot be considered high. However, this value was derived on the assumption that the introduced fuel was burnt up in the cell. If the result involves the

consumption level of the fuel in the cell, the conversion efficiency could drastically become higher.

[0053]

[Hydrogen generating example 3]

The same hydrogen generating cell as that of hydrogen generating example 1 was used. The temperature of the cell was kept at 70°C, and fuel at a fuel concentration of 0.5, 1 or 2M was applied at a constant flow rate of 8 ml/min. Then, relations of the flow rate of fuel, the flow rate of air, the evolution volume of gas and open-circuit voltage with the flow rate of air are shown in FIG. 7.

From the graph it was found that as the concentration of fuel decreases, the evolution volume of gas becomes larger.

[0054]

FIG. 8 shows a graph for indicating relationship between the open-circuit voltage and the evolution volume of gas, both adapted from the results of FIG. 7.

From this, it was found that the evolution volume of gas depends on the open-circuit voltage, and that gas evolves when the open-circuit voltage is in the range of 300 to 600 mV. The evolution volume of gas is the highest around 450 mV for all the fuel concentrations tested as in hydrogen generating example 1.

[0055]

[Hydrogen generating example 4]

Next, effect of the thickness of electrolyte membrane on the evolution volume of gas was studied.

The hydrogen generating cell was constructed similarly to the above examples, using a Nafion 112 (Dupont) having a

thickness of 50 μm, instead of Nafion 115 (Dupont) having a thickness of 130 μm as used in the above examples 1 to 3. The cell was operated: temperature at 70°C; concentration of fuel at 1M; and flow rate of fuel at 8 ml/min, and relations of the flow rate of fuel, the flow rate of air, the evolution volume of gas and open-circuit voltage with the flow rate of air were studied.

Both Nafion 115 and 112 membranes are made of the same material as a single difference in their thickness. Thus, only the thickness of electrolyte membranes serves as a parameter to be studied in the experiment. The study results are summarized in FIG. 9.

From this, it was found that the evolution volume of gas was similar regardless of the thickness of electrolyte membrane.

[0056]

FIG. 10 shows a graph for indicating relationship between the open-circuit voltage and the evolution volume of gas, both adapted from the results of FIG. 9. As seen from the figure, the evolution volume of gas depends on the open-circuit voltage, and is the highest around 450 mV.

[0057]

[Hydrogen generating example 5]

The structure of a hydrogen generating cell with means for withdrawing electric energy is outlined in FIG. 11.

The hydrogen generating cell of this example is the same in structure as that of hydrogen generating example 1 except that the cell comprises a fuel electrode as a negative electrode and an air electrode as a positive electrode with

means for withdrawing electric energy.

The hydrogen generating cell was placed in an electric furnace where hot air was circulated. The cell was operated while the temperature thereof being kept at 50°C with the flow rate of air to the air electrode kept at 10 to 90 ml/min and the flow of 1M aqueous solution of methanol (fuel) to the fuel electrode kept at 5 ml/min to cause gas to evolve. Then, while the external current flowing between the air electrode and the fuel electrode being varied, the operation voltage between the fuel electrode and the air electrode, the volume of gas evolved from the fuel electrode and gas composition were monitored and analyzed.

[0058]

Relation of the operation voltage with the current density withdrawn revealed in the test is shown in FIG. 12.

It was found that as the flow rate of air is reduced, the dischargeable limit current density becomes smaller with the reduction of the operation voltage.

[0059]

FIG. 13 shows a graph for indicating relationship between the evolution volume of hydrogen and the operation voltage, both adapted from the results of FIG. 12.

From this, it was found that the evolution volume of hydrogen depends on the operation voltage, and gas evolves when the operation voltage is in the range of 300 to 600 mV. Moreover, when the flow rate of air is in the range of 50 to 60 ml/min, hydrogen evolves most readily.

[0060]

Next, the cell was operated under a condition of a high

gas evolution efficiency: temperature at 50°C; flow rate of fuel at 5 ml/min; flow rate of air at 50 ml/min; and current density at 8.4 mA/cm^2, which is the condition making the rate of gas evolution large, to cause gas to evolve. The concentration of hydrogen in the gas was determined by gas chromatography.

As a result, it was found that the gas contained hydrogen at about 74%, and hydrogen evolved at a rate of 5.1 ml/min.

[0061]

What is important here is that current was withdrawn outside from the hydrogen generating cell of this example. In other words, the hydrogen generating cell of the present invention converted part of fuel into hydrogen while withdrawing electric energy to outside. In addition, conversion of fuel into hydrogen occurred at a surprisingly low temperature of 30 to 70°C. In view of these facts, the hydrogen generating device of the present invention is likely to be novel.

[0062]

[Hydrogen generating example 6]

The structure of hydrogen generating cell with means for providing electric energy from outside is outlined in FIG. 14.

The hydrogen generating cell is the same in structure as that of hydrogen generating example 1 except that the cell comprises a fuel electrode as a positive electrode and an oxidizing electrode as a negative electrode with means for providing electric energy from outside.

The hydrogen generating cell was placed in an electric furnace where hot air was circulated. The cell was operated

while the temperature thereof being kept at 50°C with the flow of air to the air electrode kept at 10 to 80 ml/min and the flow of 1M aqueous solution of methanol (fuel) to the fuel electrode kept at 5 ml/min. Then, while the current flowing between the air electrode and the fuel electrode being varied by means of a DC power source from outside, the operation voltage between the fuel electrode and the air electrode, the volume of gas evolved from the fuel electrode and gas composition were monitored and analyzed.

[0063]

Relation of the rate of hydrogen evolution with the current density applied in the test is shown in FIG. 15.

It was found that the efficiency of hydrogen evolution becomes equal to or more than 100% in certain areas when the current density is kept not more than 40 mA/cm^2. This suggests that it is possible to obtain hydrogen whose energy content is larger than the electric energy supplied from outside by operating the cell in those areas.

[0064]

FIG. 16 shows a graph for indicating relationship between the evolution volume of hydrogen and the operation voltage, both adapted from the results of FIG. 15.

From this, it was found that the evolution volume of hydrogen tends to depend on the operation voltage and, when the operation voltage is equal to or larger than 600 mV, becomes virtually constant, and hydrogen is readier to evolve with reduction of the flow rate of air.

[0065]

Relation of the operation voltage with the current

density applied is shown in FIG. 17.

The areas in FIG. 15 where the efficiency of hydrogen evolution is 100% or more fall below the line defined by the operation voltage being equal to or lower than 600 mV in FIG. 17.

[0066]

Next, the cell was operated under a condition of the highest gas evolution efficiency: temperature at 50°C; flow rate of fuel at 5 ml/min; flow rate of air at 50 ml/min; and current density at 4.8 mA/cm^2 to cause gas to evolve. The concentration of hydrogen in the gas was determined by gas chromatography. As a result, it was found that the gas contained hydrogen at about 86%, and hydrogen evolved at a rate of 7.8 ml/min. The efficiency of hydrogen evolution at this time was 352% in terms of electric charge.

[0067]

What is important here is that hydrogen was withdrawn from the hydrogen generating cell of this example whose energy content exceeded the electric current supplied from outside. In other words, the hydrogen generating cell according to the present invention converts part of the fuel into hydrogen more than the electrolytic reaction by the inputted electric energy. In addition, conversion of fuel into hydrogen occurred at a surprisingly low temperature of 30 to 70°C. In view of these facts, the hydrogen generating process of the invention is likely to be novel.

As has been described, the hydrogen generating device used in the hydrogen supply system of the present invention is designed to generate a hydrogen-containing gas by decomposing

an organic-containing fuel at a temperature of 100°C or lower.

[Brief Description of Drawings]

[0068]

[FIG. 1]

A diagram for showing an example of a system flow of a hydrogen supply system of the present invention.

[FIG. 2]

A schematic diagram of a hydrogen generating cell (requiring no supply of electric energy from outside) described in hydrogen generating example 1.

[FIG. 3]

A graph for indicating relations of the evolution volume of gas and open-circuit voltage with the flow rate of air when temperature is varied (hydrogen generating example 1).

[FIG. 4]

A graph for indicating relation between the open-circuit voltage and the evolution volume of gas when temperature is varied (hydrogen generating example 1).

[FIG. 5]

A graph for indicating relations of the evolution volume of gas and open-circuit voltage with the flow rate of air when the flow rate of fuel is varied (hydrogen generating example 2).

[FIG. 6]

A graph for indicating relation between the evolution volume of gas and open-circuit voltage when the flow rate of fuel is varied (hydrogen generating example 2).

[FIG. 7]

A graph for indicating relations of the evolution volume

of gas and open-circuit voltage with the flow rate of air when the concentration of fuel is varied (hydrogen generating example 3).

[FIG. 8]

A graph for indicating relation between the open-circuit voltage and the evolution volume of gas when the concentration of fuel is varied (hydrogen generating example 3).

[FIG. 9]

A graph for indicating relations of the evolution volume of gas and open-circuit voltage with the flow rate of air when the thickness of electrolyte membrane is varied (hydrogen generating example 4).

[FIG. 10]

A graph for indicating relation between the open-circuit voltage and the evolution volume of gas when the thickness of electrolyte membrane is varied (hydrogen generating example 4).

[FIG. 11]

A schematic diagram of a hydrogen generating cell (for withdrawing electric energy) described in hydrogen generating example 5.

[FIG. 12]

A graph for indicating relation between the operation voltage and the current density withdrawn when the flow rate of air is varied.

[FIG. 13]

A graph for indicating relation (discharging) between the evolution volume of hydrogen and the operation voltage when the flow rate of air is varied.

[FIG. 14]

A schematic diagram of a hydrogen generating cell (providing external electric energy from outside) described in hydrogen generating example 6.

[FIG. 15]

A graph for indicating relation between the rate of hydrogen evolution and the current density applied when the flow rate of air is varied.

[FIG. 16]

A graph for indicating relation (charging) between the evolution volume of hydrogen and operation voltage when the flow rate of air is varied.

[FIG. 17]

A graph for indicating relation between the operation voltage and the current density applied when the flow rate of air is varied.

[Document] Claims:

[Claim 1]

A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, said system characterized in that

the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound at a temperature of 100°C or lower.

[Claim 2]

The hydrogen supply system according to claim 1, characterized in that

the hydrogen generating device produces a hydrogen-containing gas by decomposing a fuel containing an organic compound at a temperature of 30 to 70°C.

[Claim 3]

The hydrogen supply system according to claim 1 or 2, characterized in that

the hydrogen generating device produces a hydrogen-containing gas without supplying electric energy from outside to a hydrogen generating cell composed of a partition membrane.

[Claim 4]

The hydrogen supply system according to claim 1 or 2, characterized in that

the hydrogen generating device produces a hydrogen-containing gas while withdrawing electric energy from a hydrogen generating cell composed of a partition membrane.

[Claim 5]

The hydrogen supply system according to claim 1 or 2, characterized in that

the hydrogen generating device produces a hydrogen-containing gas while providing electric energy from outside to a hydrogen generating cell composed of a partition membrane.

[Claim 6]

A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, said system characterized in that

the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound and comprises a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the organic compound, and means for supplying an oxygen-containing gas on the other surface of the partition membrane.

[Claim 7]

The hydrogen supply system according to claim 6, characterized in that

the hydrogen generating device has no means for supplying electric energy from outside to a hydrogen generating cell constituting the hydrogen generating device.

[Claim 8]

The hydrogen supply system according to claim 6 or 7, characterized in that

the hydrogen generating device is provided with an oxidizing electrode on a surface of the partition membrane

supplying an oxygen-containing gas.

[Claim 9]

A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, said system characterized in that

the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound and comprises a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the organic compound, an oxidizing electrode provided on the other surface of the partition membrane, means for supplying an oxygen-containing gas to the oxidizing electrode, and means for withdrawing electric energy with the fuel electrode serving as a negative electrode and the oxidizing electrode as a positive electrode.

[Claim 10]

A hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, said system characterized in that

the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound and comprises a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the

organic compound, an oxidizing electrode provided on the other surface of the partition membrane, means for supplying an oxygen-containing gas to the oxidizing electrode, and means for providing electric energy from outside with the fuel electrode serving as a positive electrode and the oxidizing electrode as a negative electrode.

[Claim 11]

The hydrogen supply system according to any one of claims 8 to 10, characterized in that

the hydrogen generating device adjusts the evolution volume of the hydrogen-containing gas by controlling an open-circuit voltage or an operation voltage between the fuel electrode and the oxidizing electrode.

[Claim 12]

The hydrogen supply system according to claim 11, characterized in that

the open-circuit voltage or operation voltage is adjusted to 300 to 600 mV.

[Claim 13]

The hydrogen supply system according to claim 11 or 12, characterized in that

the open-circuit voltage or operation voltage is adjusted by controlling the supply volume of the oxygen-containing gas.

[Claim 14]

The hydrogen supply system according to any one of claims 11 to 13, characterized in that

the open-circuit voltage or operation voltage is adjusted by controlling the concentration of oxygen in the oxygen-containing gas.

[Claim 15]

The hydrogen supply system according to any one of claims 11 to 14, characterized in that

the open-circuit voltage or operation voltage is adjusted by controlling the supply volume of the fuel containing an organic compound.

[Claim 16]

The hydrogen supply system according to any one of claims 11 to 15, characterized in that

the open-circuit voltage or operation voltage is adjusted by controlling the concentration of the fuel containing an organic compound.

[Claim 17]

The hydrogen supply system according to any one of claims 11 to 16, characterized in that

the open-circuit voltage or operation voltage is adjusted by controlling the electric energy to be provided or the electric energy to be withdrawn.

[Claim 18]

The hydrogen supply system according to any one of claims 6 to 17, characterized in that

the partition membrane is a proton conducting solid electrolyte membrane.

[Claim 19]

The hydrogen supply system according to claim 18, characterized in that

the proton conducting solid electrolyte membrane is a perfluorocarbon sulfonate-based solid electrolyte membrane.

[Claim 20]

The hydrogen supply system according to any one of claims 6 to 17, characterized in that

the partition membrane is an oxygen-soluble polymer membrane.

[Claim 21]

The hydrogen supply system according to any one of claims 6 to 20, characterized in that

a catalyst of the fuel electrode is made of platinum-ruthenium alloy supported by carbon powder serving as a base.

[Claim 22]

The hydrogen supply system according to any one of claims 8 to 21, characterized in that

a catalyst of the oxidizing electrode is made of platinum supported by carbon powder serving as a base.

[Claim 23]

The hydrogen supply system according to any one of claims 1 to 22, characterized in that

the fuel containing an organic compound is an aqueous solution containing methanol.

[Claim 24]

The hydrogen supply system according to any one of claims 1 to 23, characterized by comprising

means for circulating the fuel containing an organic compound.

[Claim 25]

The hydrogen supply system according to any one of claims 1 to 24, characterized in that

a carbon dioxide absorbing portion for absorbing carbon dioxide contained in the generated hydrogen-containing gas.

[Document] Abstract

[Abstract]

[Object]

With a view to give a solution to the above problems, the present invention aims to provide a hydrogen supply system using a hydrogen generating device which can easily supply hydrogen to a hydrogen storage container loaded on a fuel cell automobile, produce a hydrogen-containing gas at a low temperature, and moreover, requires no large electric energy.

[Means for Achieving the Object]

There is provided a hydrogen supply system provided with hydrogen supply means for supplying hydrogen to a hydrogen storage container loaded on a fuel cell automobile and a hydrogen generating device producing hydrogen-containing gas to be supplied to the hydrogen supply means, the system. In the system, the hydrogen generating device produces the hydrogen-containing gas by decomposing a fuel containing an organic compound at a temperature of 100°C or lower. Further, the hydrogen generating device includes a partition membrane, a fuel electrode provided on one surface of the partition membrane, means for supplying the fuel electrode with the fuel containing the organic compound, and means for supplying an oxygen-containing gas on the other surface of the partition membrane. Moreover, the hydrogen generating device includes means for withdrawing electric energy with the fuel electrode serving as a negative electrode and an oxidizing electrode (provided on the surface of the partition membrane to supply the oxygen-containing gas) serving as a positive electrode, and means for providing electric energy from outside with the

fuel electrode serving as a positive electrode and the oxidizing electrode as a negative electrode.

[Elected figure] FIG. 1

FIG. 1

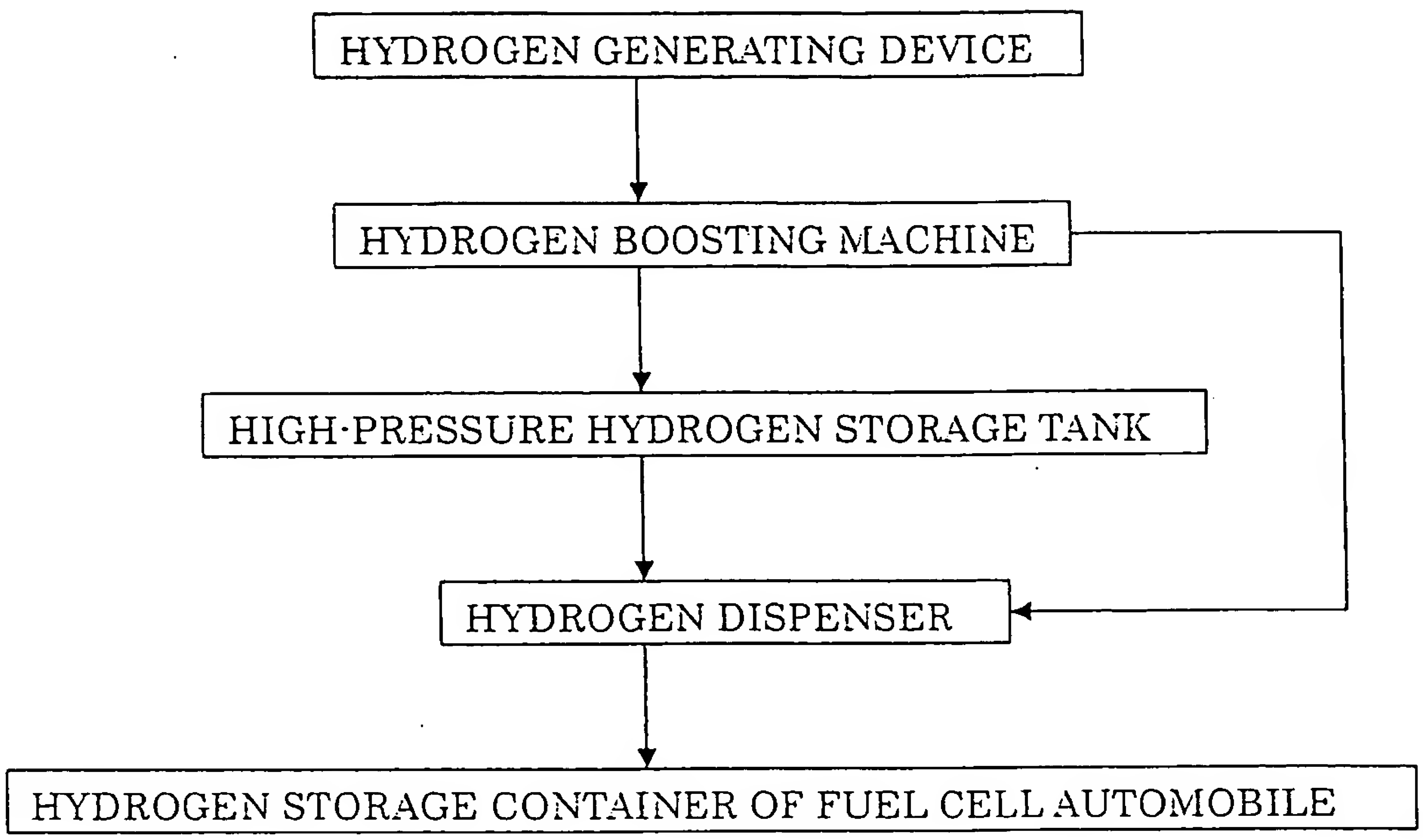

HYDROGEN GENERATING DEVICE
HYDROGEN BOOSTING MACHINE
HIGH-PRESSURE HYDROGEN STORAGE TANK
HYDROGEN DISPENSER
HYDROGEN STORAGE CONTAINER OF FUEL CELL AUTOMOBILE

FIG. 2

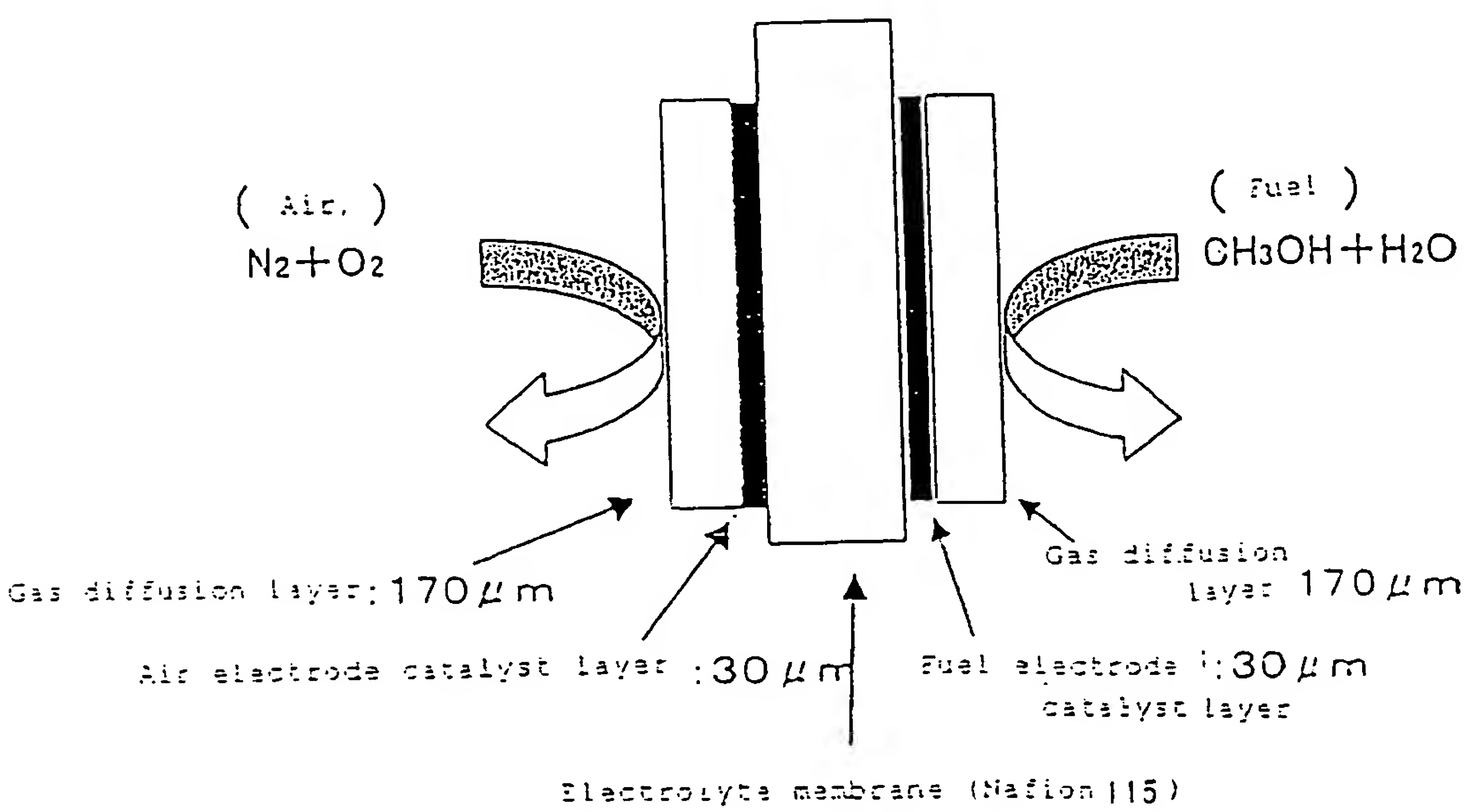

(Air)
N_2+O_2
(Fuel)
CH_3OH+H_2O
Gas diffusion layer: 170 μm
Gas diffusion layer 170 μm
Air electrode catalyst layer :30 μm
Fuel electrode :30 μm catalyst layer
Electrolyte membrane (Nafion 115)

FIG. 3

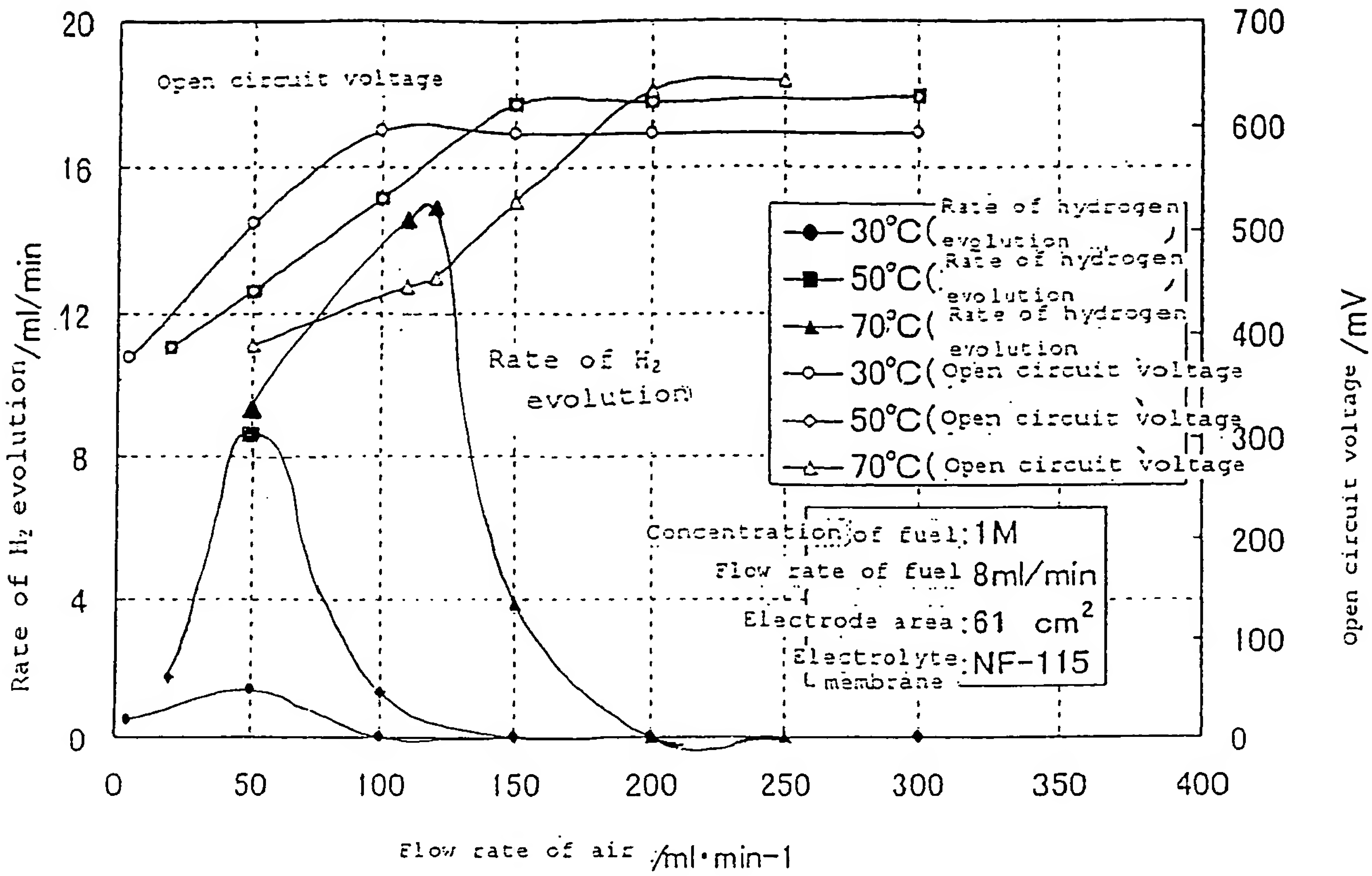

Open circuit voltage
Rate of H_2 evolution
30°C (Rate of hydrogen evolution)
50°C (Rate of hydrogen evolution)
70°C (Rate of hydrogen evolution)
30°C (Open circuit voltage)
50°C (Open circuit voltage)
70°C (Open circuit voltage)
Concentration of fuel: 1M
Flow rate of fuel 8ml/min
Electrode area: 61 cm²
Electrolyte membrane: NF-115
Rate of H_2 evolution/ml/min
Open circuit voltage /mV
Flow rate of air /ml·min-1
0
4
8
12
16
20
0
100
200
300
400
500
600
700
0
50
100
150
200
250
300
350
400

FIG. 4

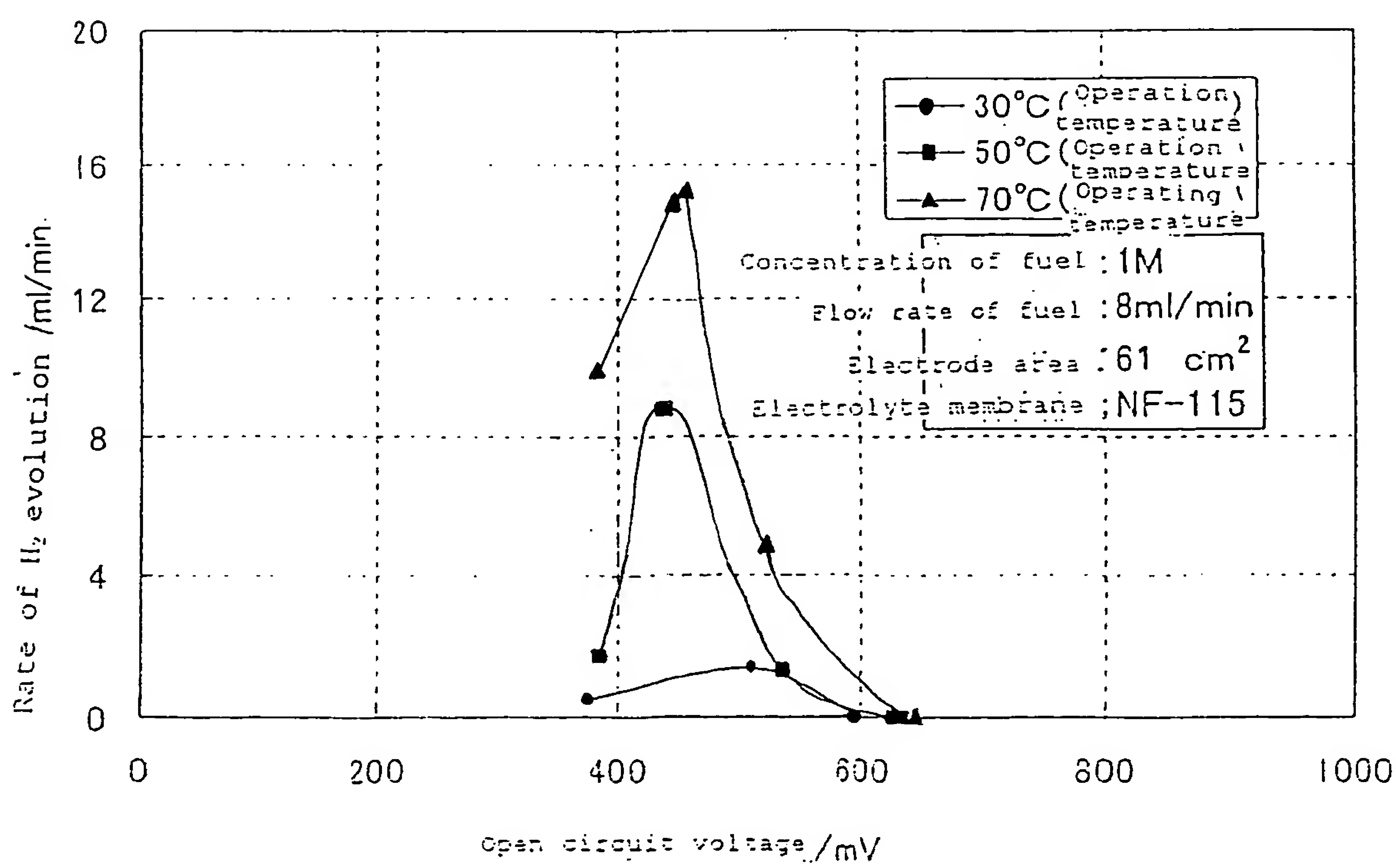
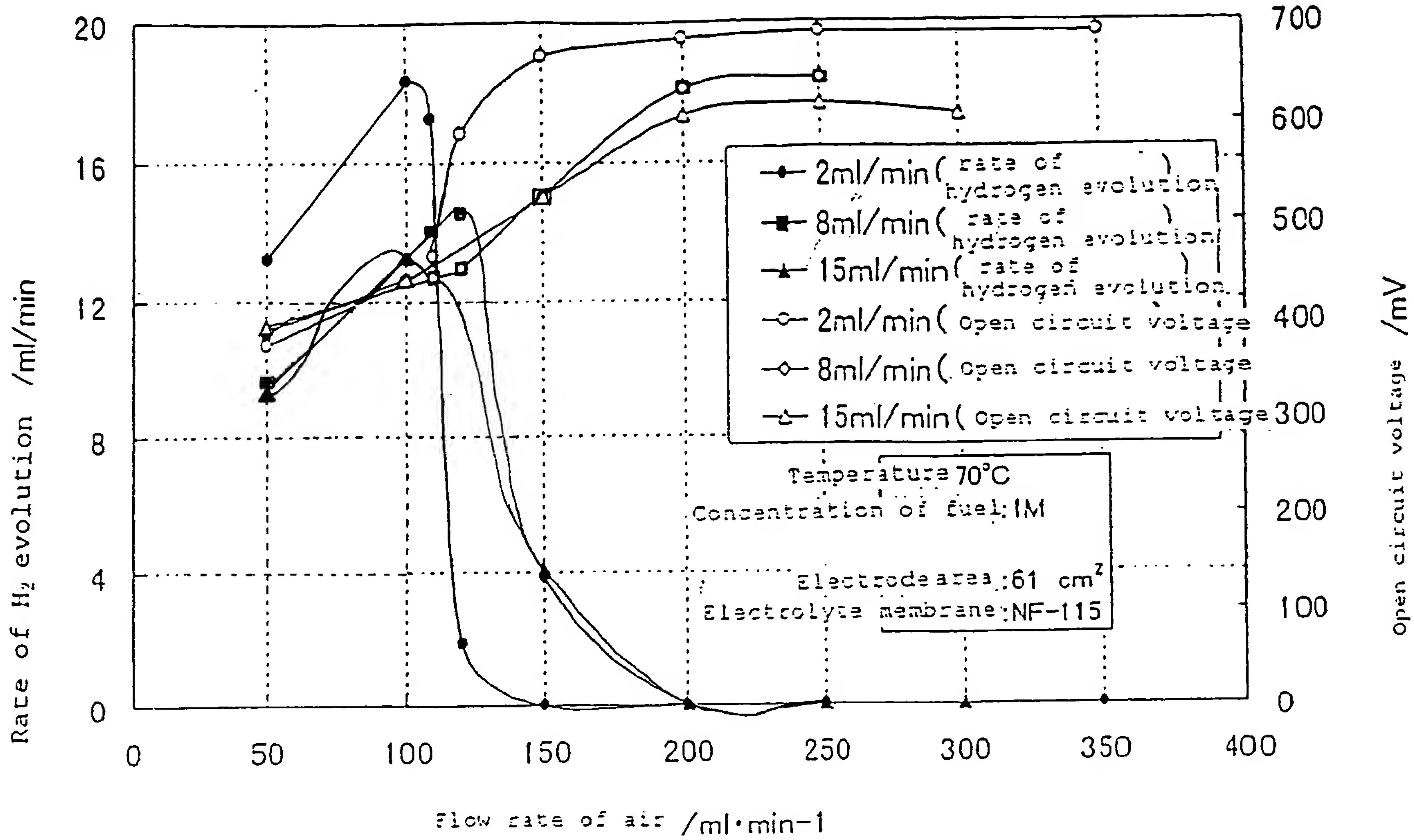
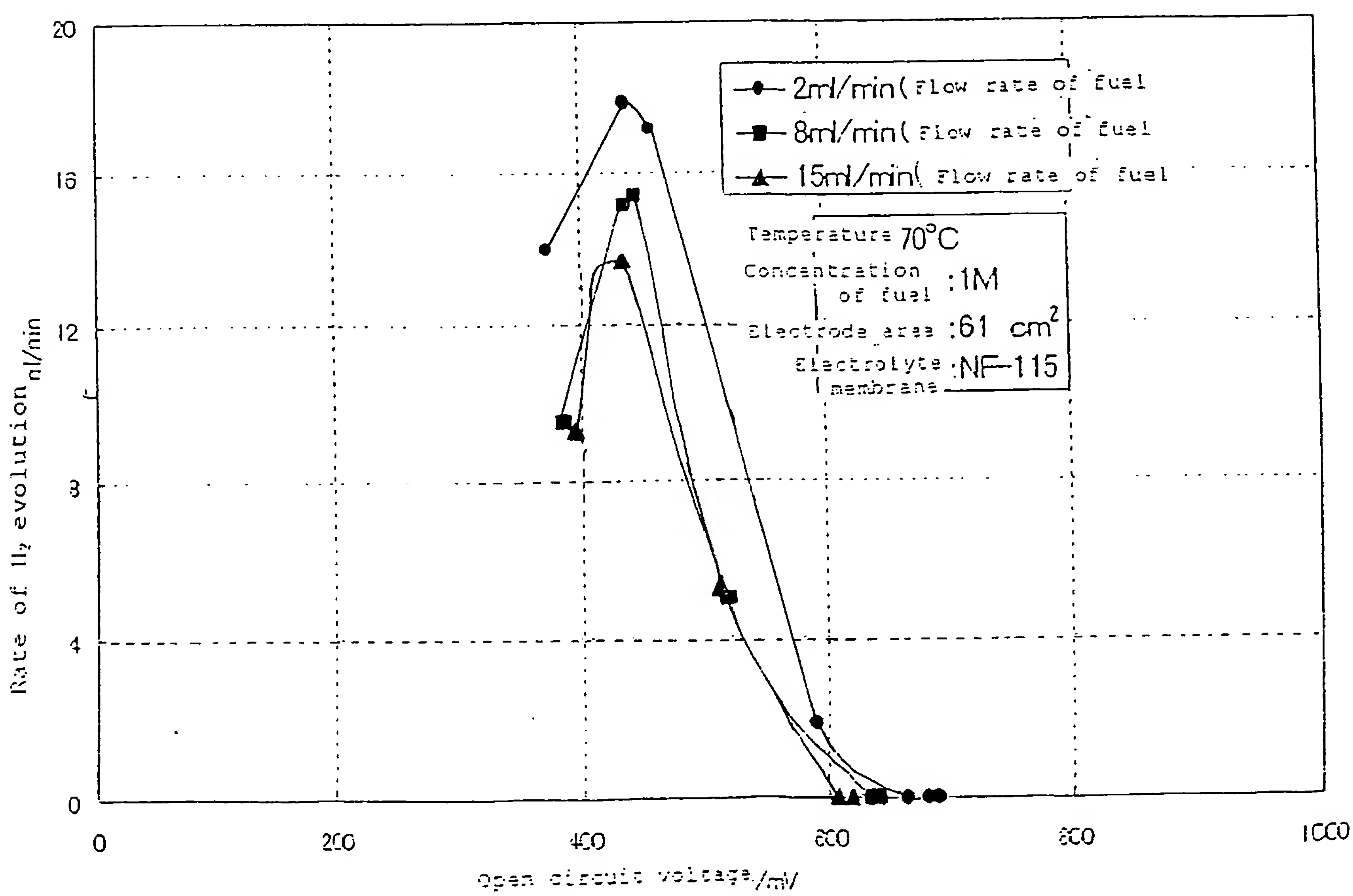

30°C (Operation temperature)
50°C (Operation temperature)
70°C (Operating temperature)
Concentration of fuel: 1M
Flow rate of fuel: 8ml/min
Electrode area: 61 cm²
Electrolyte membrane; NF-115
Rate of H_2 evolution /ml/min
Open circuit voltage /mV
0
4
8
12
16
20
0
200
400
600
800
1000

FIG. 5



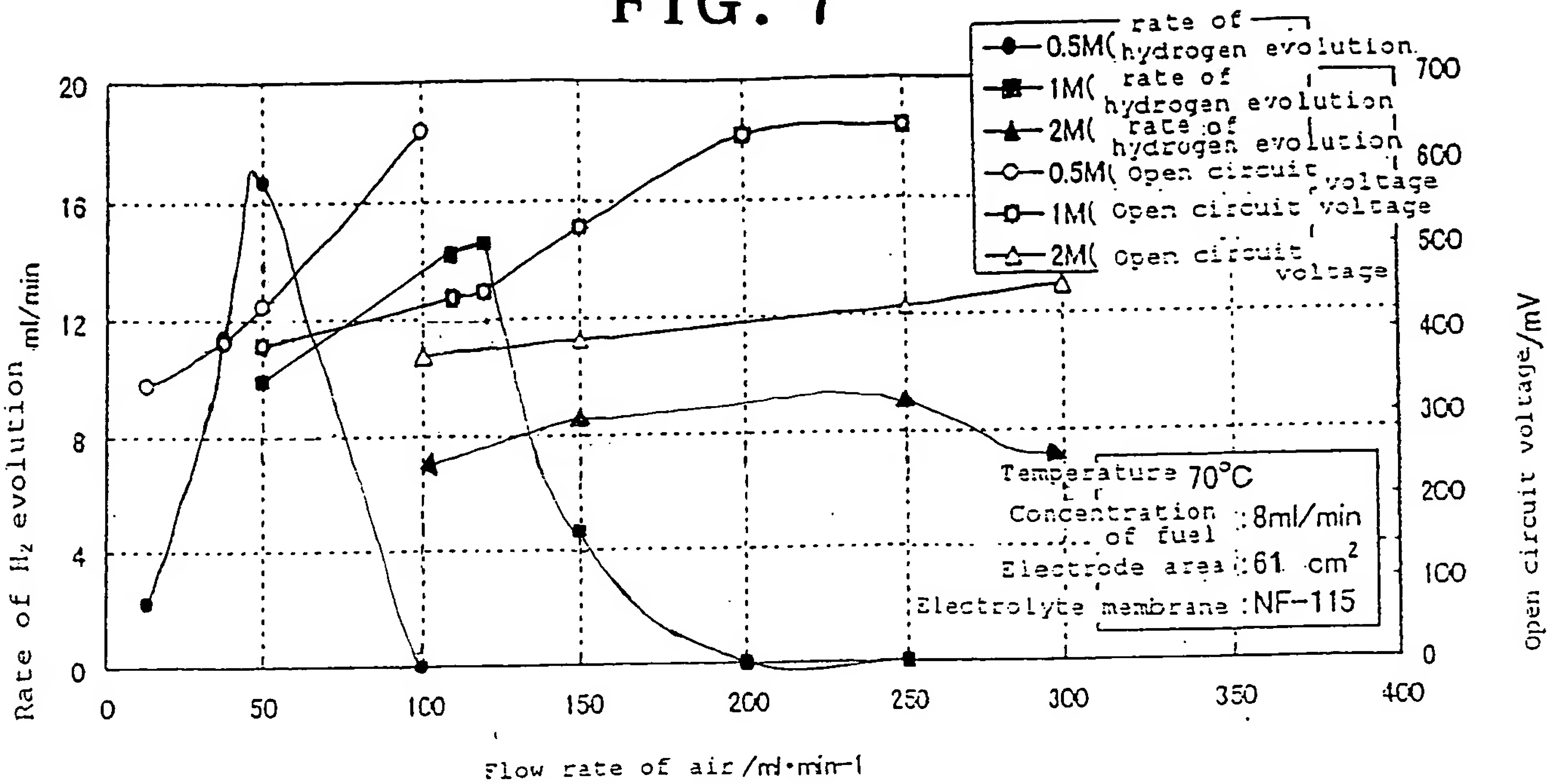
2ml/min(rate of hydrogen evolution)
8ml/min(rate of hydrogen evolution)
15ml/min(rate of hydrogen evolution)
2ml/min(open circuit voltage
8ml/min(open circuit voltage
15ml/min(open circuit voltage
Temperature 70°C
Concentration of fuel:1M
Electrode area :61 cm²
Electrolyte membrane:NF-115
Rate of H₂ evolution /ml/min
Open circuit voltage /mV
Flow rate of air /ml·min-1

FIG. 6



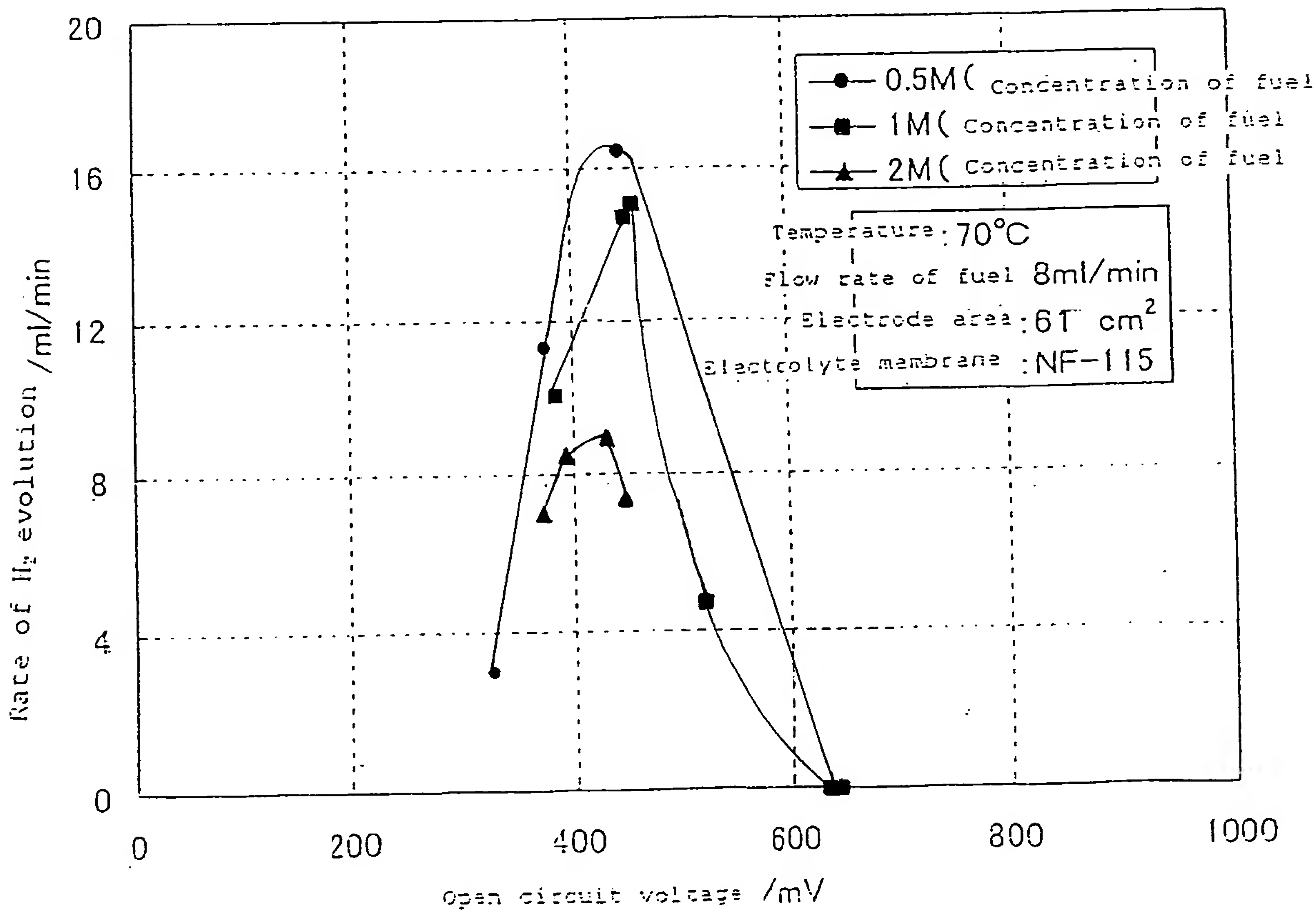
2ml/min(Flow rate of fuel
8ml/min(Flow rate of fuel
15ml/min(Flow rate of fuel
Temperature 70°C
Concentration of fuel :1M
Electrode area :61 cm²
Electrolyte membrane :NF-115
Rate of H₂ evolution ml/min
Open circuit voltage /mV

FIG. 7



0.5M(rate of hydrogen evolution
1M(rate of hydrogen evolution
2M(rate of hydrogen evolution
0.5M(open circuit voltage
1M(open circuit voltage
2M(open circuit voltage
Temperature 70°C
Concentration of fuel :8ml/min
Electrode area :61 cm²
Electrolyte membrane :NF-115
Rate of H₂ evolution ml/min
open circuit voltage/mV
Flow rate of air /ml·min-1
0
50
100
150
200
250
300
350
400
4
8
12
16
20
100
200
300
400
500
600
700

FIG. 8



0.5M(concentration of fuel
1M(concentration of fuel
2M(concentration of fuel
Temperature : 70°C
Flow rate of fuel 8ml/min
Electrode area : 61 cm²
Electrolyte membrane : NF-115
Rate of H₂ evolution /ml/min
open circuit voltage /mV
0
4
8
12
16
20
200
400
600
800
1000

FIG. 9

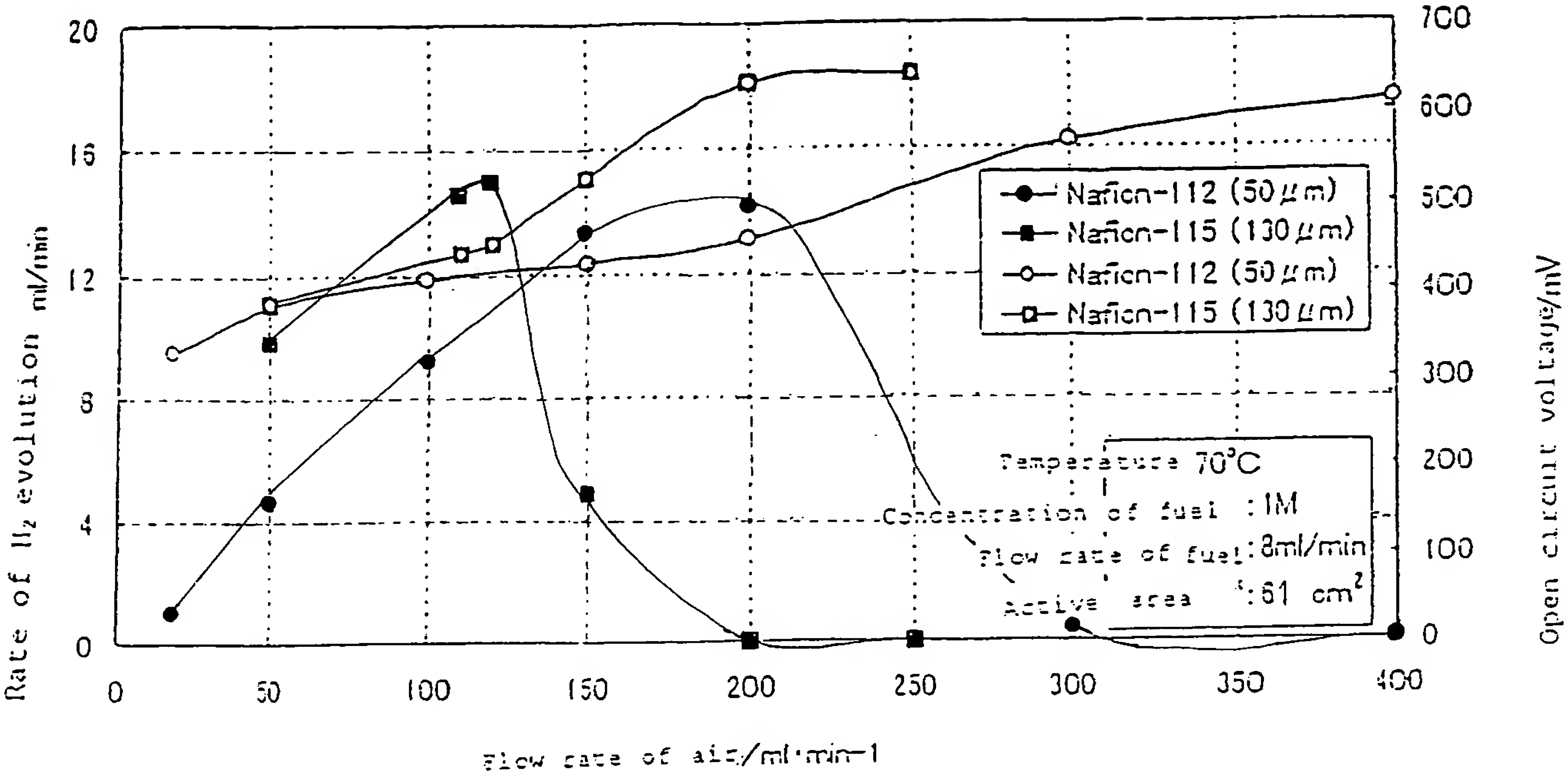

Nafion-112 (50 μm)
Nafion-115 (130 μm)
Nafion-112 (50 μm)
Nafion-115 (130 μm)
Temperature 70°C
Concentration of fuel : 1M
Flow rate of fuel : 8ml/min
Active area : 61 cm²
Rate of H₂ evolution ml/min
Open circuit voltage/mV
Flow rate of air/ml·min-1
20
16
12
8
4
0
700
600
500
400
300
200
100
0
50
100
150
200
250
300
350
400

FIG. 10

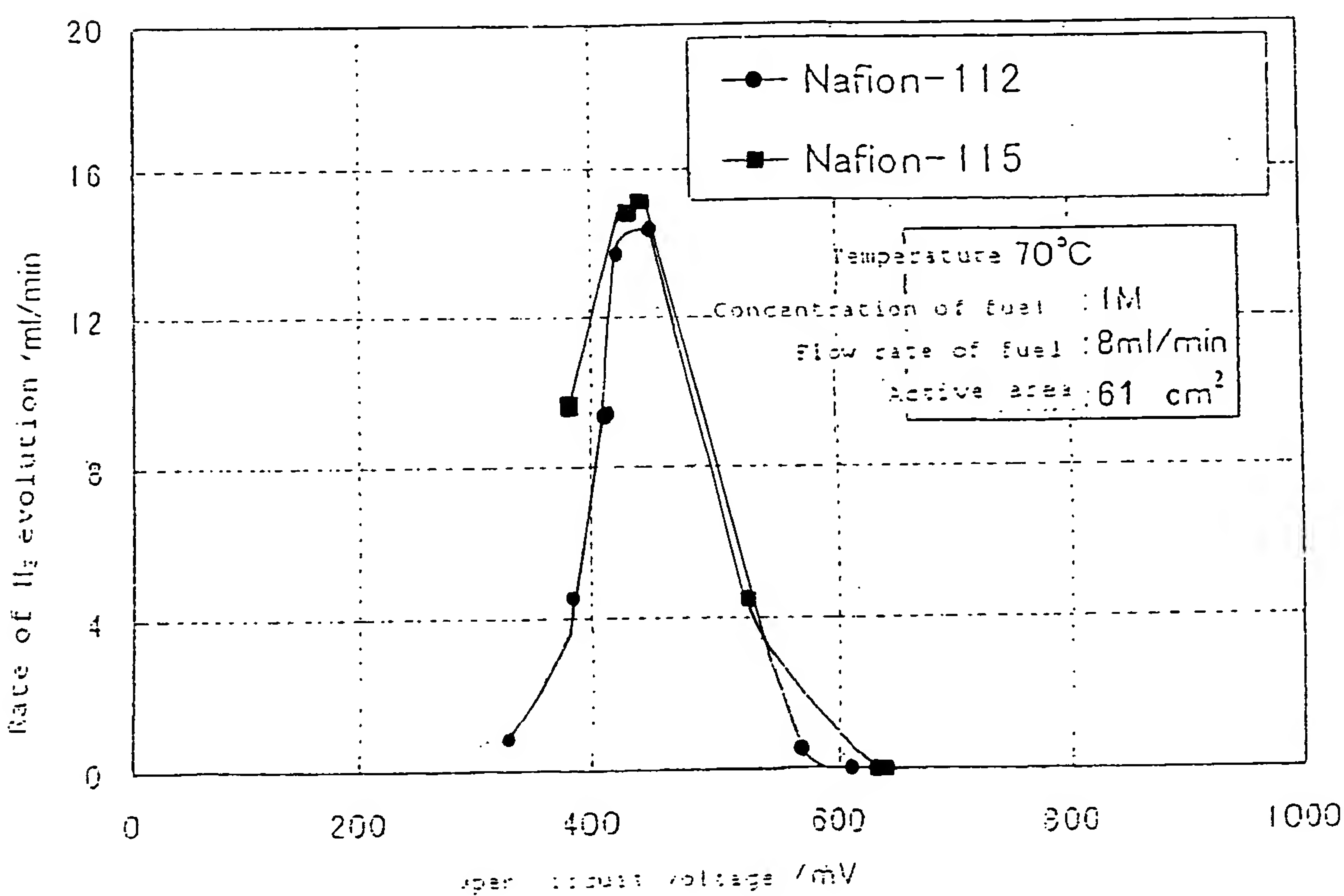
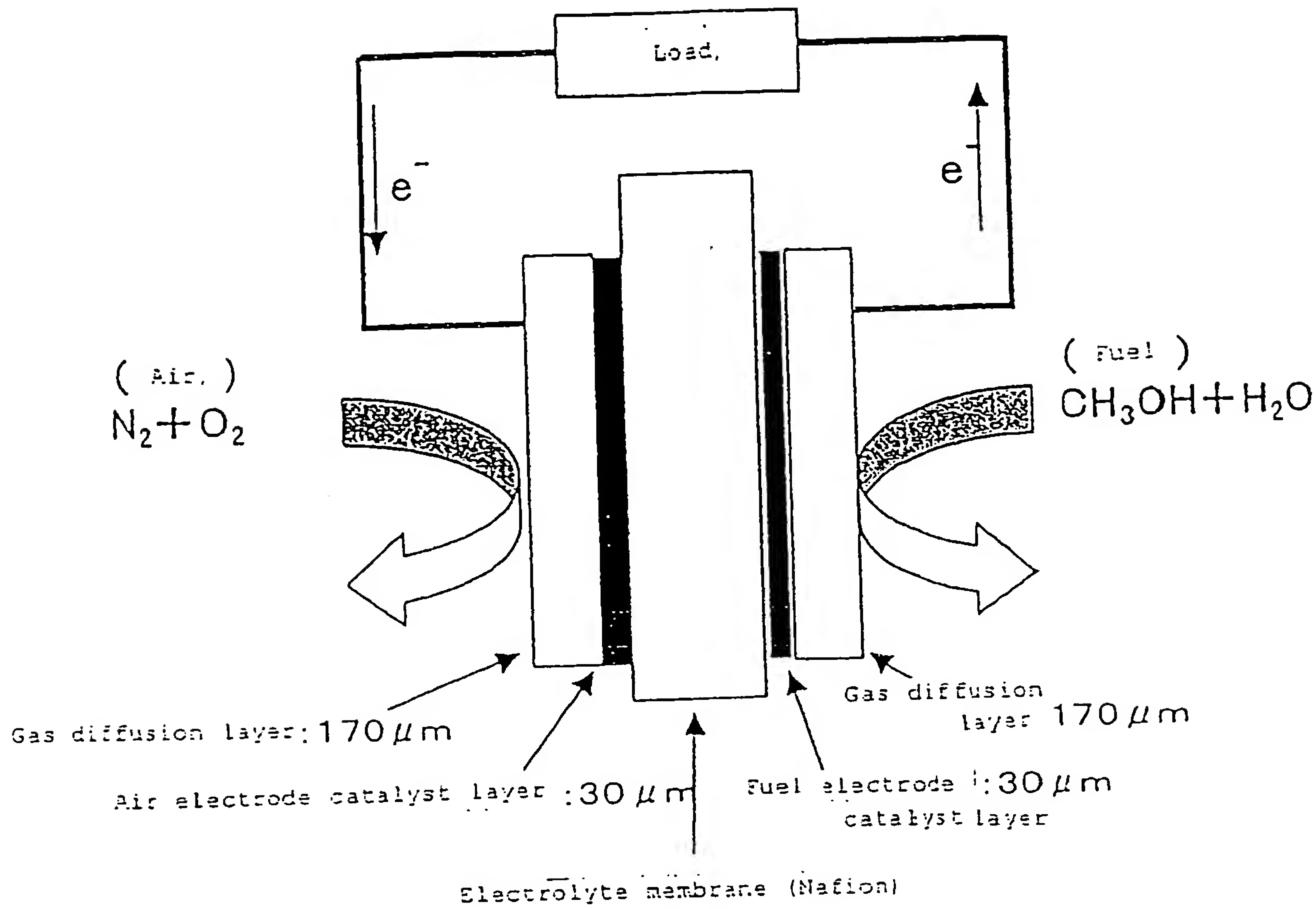
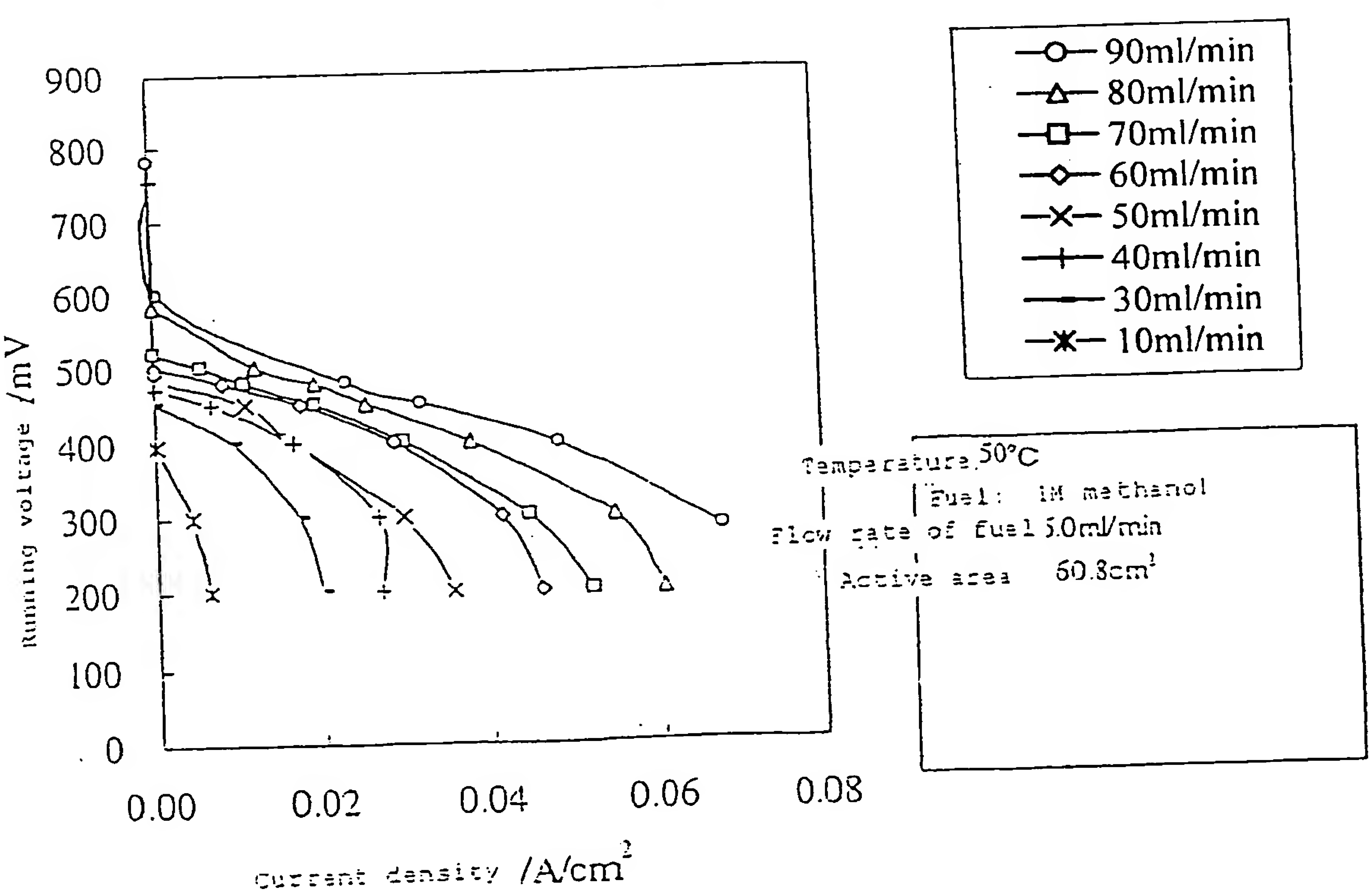

Nafion-112
Nafion-115
Temperature 70°C
Concentration of fuel : 1M
Flow rate of fuel : 8ml/min
Active area : 61 cm²
Rate of H₂ evolution /ml/min
Open circuit voltage /mV
20
16
12
8
4
0
200
400
600
800
1000

FIG. 11



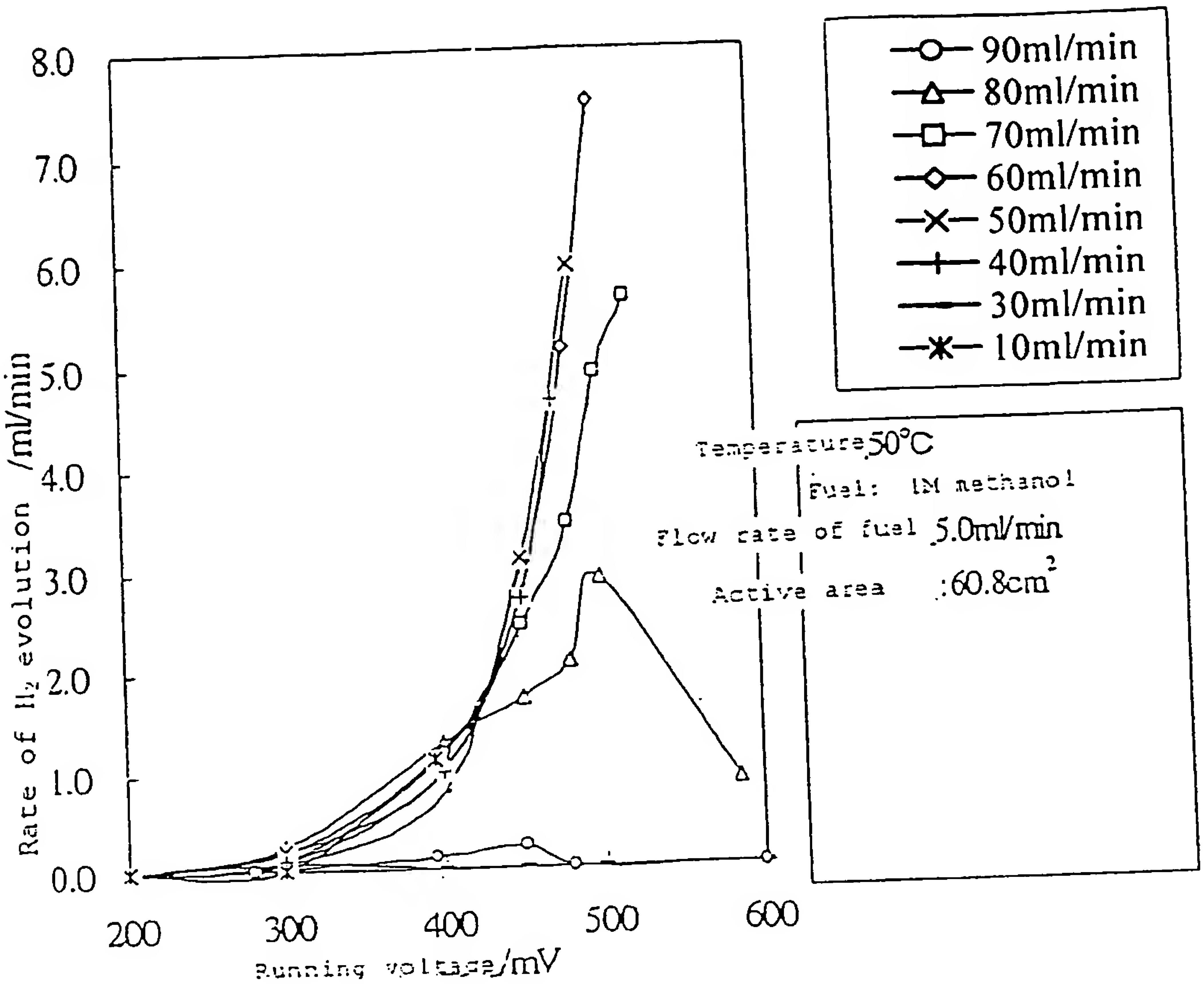
Load.
e⁻
e⁻
(Air.)
N_2+O_2
(Fuel)
CH_3OH+H_2O
Gas diffusion layer: 170 μm
Air electrode catalyst layer :30 μm
Gas diffusion layer 170 μm
Fuel electrode catalyst layer :30 μm
Electrolyte membrane (Nafion)

FIG. 12



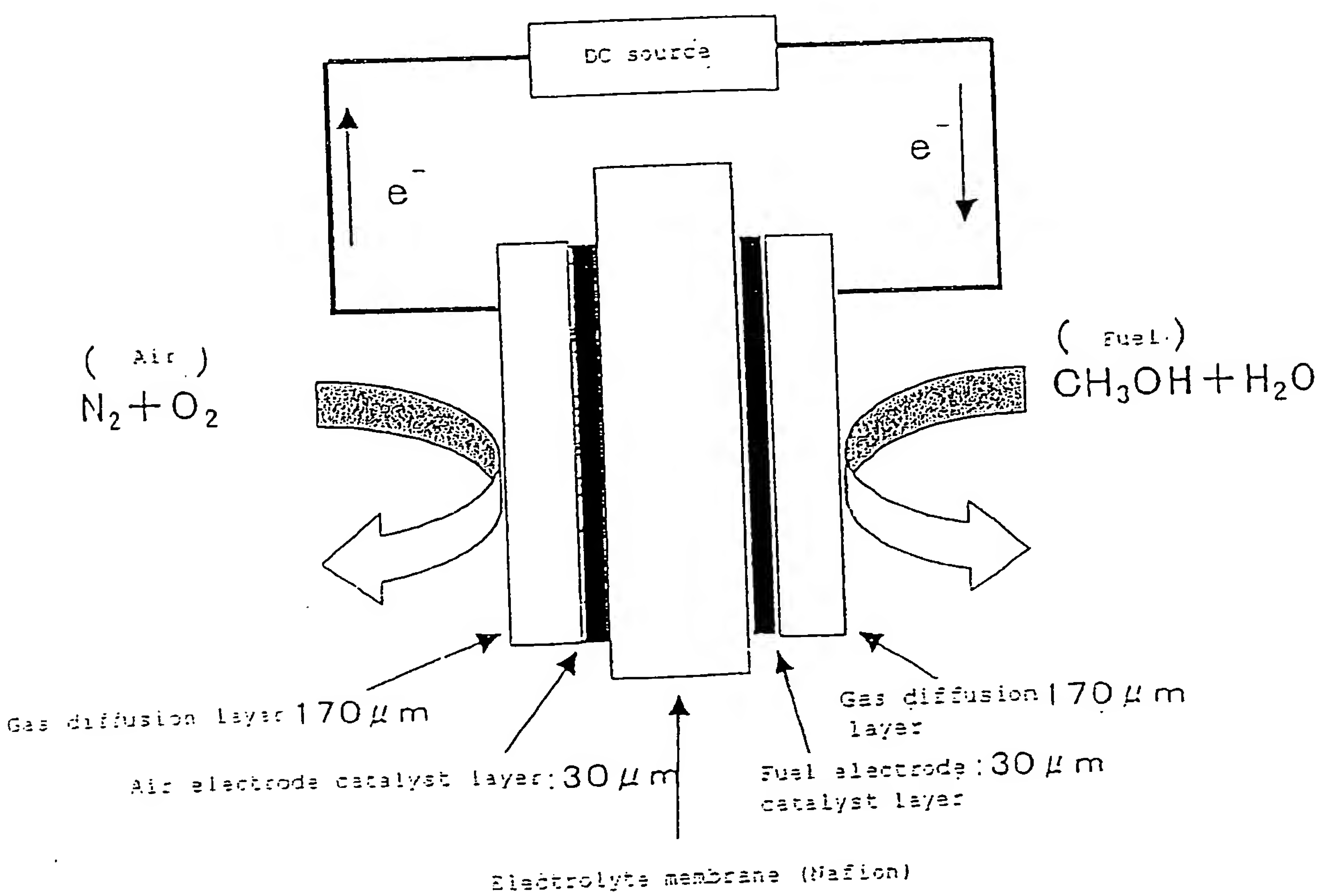
900
800
700
600
500
400
300
200
100
0
Running voltage /mV
0.00
0.02
0.04
0.06
0.08
Current density /A/cm²
90ml/min
80ml/min
70ml/min
60ml/min
50ml/min
40ml/min
30ml/min
10ml/min
Temperature 50°C
Fuel: 1M methanol
Flow rate of fuel 5.0ml/min
Active area 60.8cm²

FIG. 13



8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Rate of H_2 evolution /ml/min
200
300
400
500
600
Running voltage/mV
90ml/min
80ml/min
70ml/min
60ml/min
50ml/min
40ml/min
30ml/min
10ml/min
Temperature 50°C
Fuel: 1M methanol
Flow rate of fuel 5.0ml/min
Active area :60.8cm^2

FIG. 14



DC source
e^-
e^-
(Air)
N_2+O_2
(Fuel)
CH_3OH+H_2O
Gas diffusion layer 170 μm
Air electrode catalyst layer: 30 μm
Gas diffusion layer 170 μm
Fuel electrode catalyst layer : 30 μm
Electrolyte membrane (Nafion)

FIG. 15

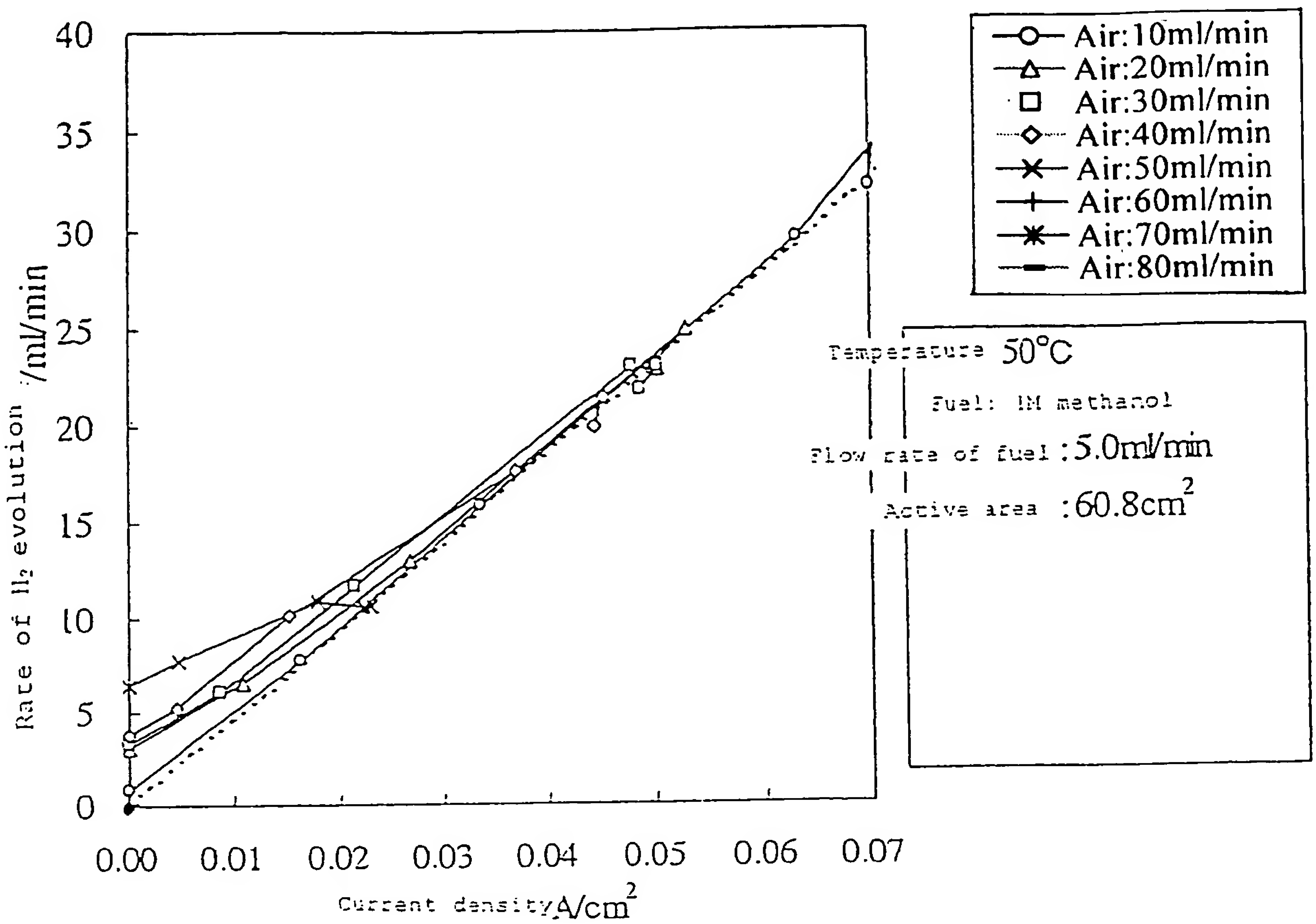

Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:60ml/min
Air:70ml/min
Air:80ml/min
Temperature 50°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm²
Rate of H₂ evolution /ml/min
Current density A/cm²
0
5
10
15
20
25
30
35
40
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07

FIG. 16

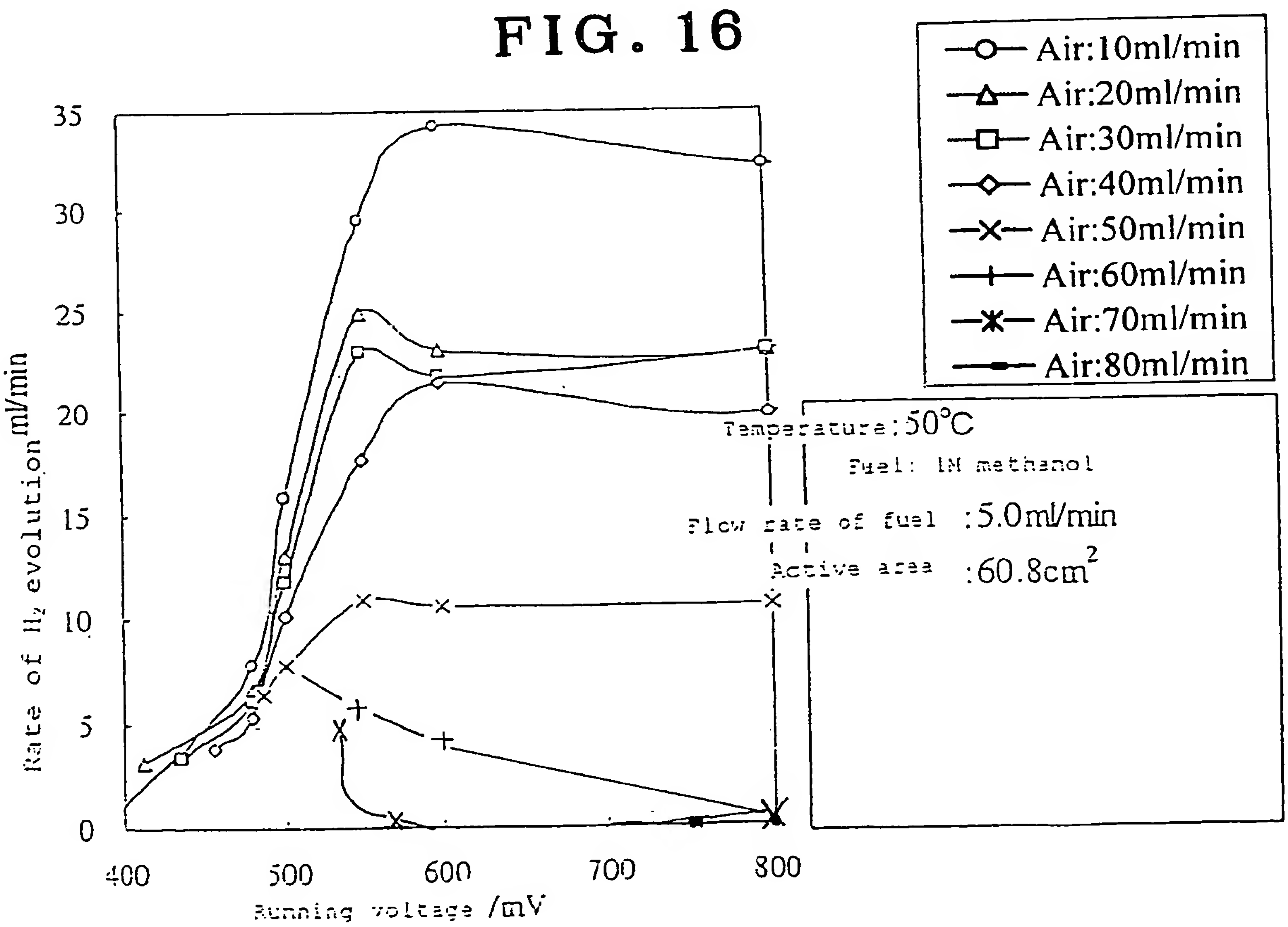
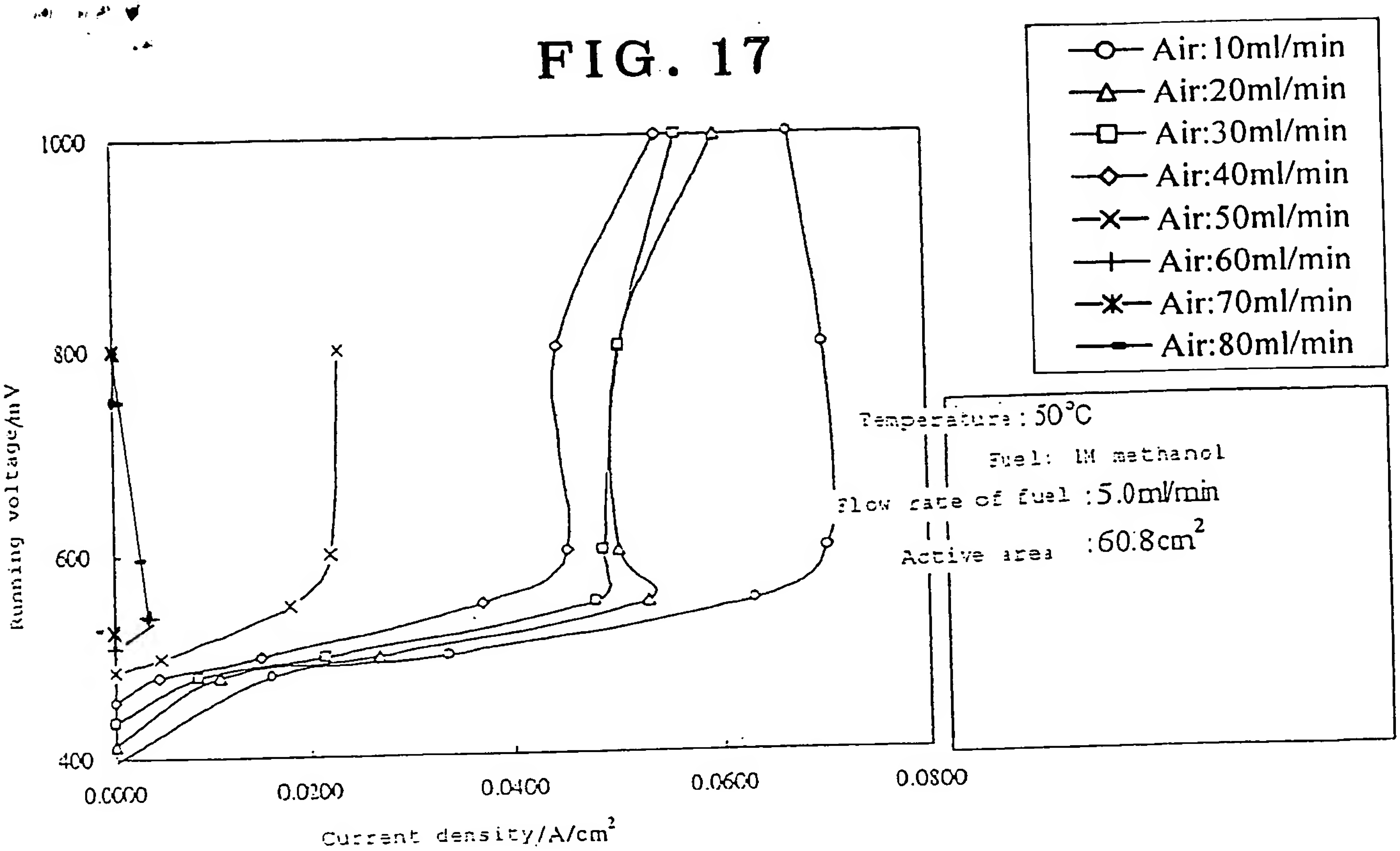

Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:60ml/min
Air:70ml/min
Air:80ml/min
Temperature:50°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm²
Rate of H₂ evolution ml/min
Running voltage /mV
0
5
10
15
20
25
30
35
400
500
600
700
800

FIG. 17



Air:10ml/min
Air:20ml/min
Air:30ml/min
Air:40ml/min
Air:50ml/min
Air:60ml/min
Air:70ml/min
Air:80ml/min
Temperature : 50°C
Fuel: 1M methanol
Flow rate of fuel :5.0ml/min
Active area :60.8cm²
1000
800
600
400
Running voltage/mV
0.0000
0.0200
0.0400
0.0600
0.0800
Current density/A/cm²